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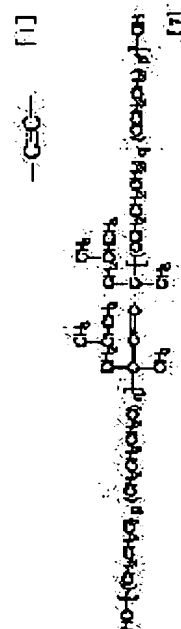
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(54) DETERGENT FOR COPPER WIRING SEMICONDUCTOR SUBSTRATE

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain a detergent capable of effectively removing impurities on the surface of a semiconductor having a copper wiring on the surface without causing corrosion and oxidation of the copper wiring and surface roughness and to provide a method for cleaning.

SOLUTION: This detergent for the surface of a semiconductor having a copper wiring on the surface comprises a nonionic surfactant containing a group of formula (1) in the molecule, for example, a nonionic surfactant of general formula 7 ($p+q+p'+q'$ is 1-20). This method for cleaning the surface of a semiconductor uses the detergent. This semiconductor having a copper wiring on the surface is obtained by treating the surface a semiconductor with the detergent.



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CLAIMS

[Claim(s)]

[Claim 1] The cleaning agent for semi-conductor front faces with which copper wiring was given to the front face which comes to contain a nonionic surfactant.

[Claim 2] A nonionic surfactant is [Formula 1] in a molecule.

A cleaning agent given in any of claim 1 which is what comes out and has the radical shown they are.

[Claim 3] A nonionic surfactant is [Formula 2] in a molecule.

A cleaning agent given in any of claim 1 which is what comes out and has the radical shown and a polyoxyalkylene group they are.

[Claim 4] The cleaning agent according to claim 3 whose polyoxyalkylene group is what is shown by the following general formula [1].

[Formula 3]

(X shows an alkylene group among a formula and y shows a positive integer.)

[Claim 5] The cleaning agent according to claim 3 whose polyoxyalkylene group is a polyoxyethylene radical or/and a polyoxypropylene radical.

[Claim 6] The cleaning agent according to claim 1 whose nonionic surfactant is what is shown by the following general formula [2].

[Formula 4]

X1 shows a low-grade alkylene group among [type, n shows a positive integer, R1 and R2 show independently a hydrogen atom, a hydroxyl group, an alkyl group, or a hydroxyalkyl radical, respectively, and R5 shows the radical shown by a hydrogen atom, the hydroxyl group, the alkyl group, the hydroxyalkyl radical, or the following general formula [3].

[Formula 5]

(R3 and R4 show independently a hydrogen atom, a hydroxyl group, an alkyl group, or a hydroxyalkyl radical among a formula, respectively, X2 shows a low-grade alkylene group, and m shows a positive integer.)]

[Claim 7] It is the cleaning agent according to claim 6 whose R5 is the radical shown by the general formula [3] in a general formula [2] and n X1 and whose m X2 are ethylene or a propylene radical independently, respectively.

[Claim 8] The cleaning agent according to claim 1 whose nonionic surfactant is what is shown by the following general formula [2'].

[Formula 6]

R1 and R2 show independently a hydrogen atom, a hydroxyl group, an alkyl group, or a hydroxyalkyl radical among [type, respectively, r and s show 0 or a positive integer independently, respectively, and R5' shows the radical shown by a hydrogen atom, the hydroxyl group, the alkyl group, the hydroxyalkyl radical, or the following general formula [3'].

[Formula 7]

(R3 and R4 show independently a hydrogen atom, a hydroxyl group, an alkyl group, or a hydroxyalkyl radical among a formula, respectively, and r' and s' show 0 or a positive integer independently, respectively.) However, r, s, r', and s' remove the case of 0 to coincidence.]

[Claim 9] The cleaning agent according to claim 1 whose nonionic surfactant is what is shown by the following general formula [2"].

[Formula 8]

(R1, R2, R3, R4, r, r', s, and s' is the same as the above among a formula.)

[Claim 10] The cleaning agent according to claim 1 whose nonionic surfactant is what is chosen from the compound shown by the following general formula [6], [7], or [8].

[Formula 9]

(p+p' is 1-20 among a formula.)

[Formula 10]

(p+q+p'+q' is 1-20 among a formula.)

[Formula 11]

(q+q' is 1-20 among a formula.)

[Claim 11] A cleaning agent given in any of claims 1-10 which are alkalinity they are.

[Claim 12] Furthermore, a cleaning agent given in any of claims 1-11 which come to

contain a nitrogen-containing alkalinity compound they are.

[Claim 13] The cleaning agent according to claim 12 with which a nitrogen-containing alkalinity compound is chosen from ammonia, primary amine, the second class amine, the third class amine, or the fourth class ammonium.

[Claim 14] The cleaning agent according to claim 13 the fourth class ammonium of whose is the fourth class ammonium shown by the following general formula [5].

[Formula 12]

(R6-R9 show among a formula the hydrocarbon residue which may have the hydroxyl group independently, respectively, and M- shows an anion.)

[Claim 15] The cleaning agent according to claim 14 which is that the fourth class ammonium shown by the general formula [5] is indicated to be by the following general formula [5'].

[Formula 13]

(R6-R9 show independently the low-grade alkyl group of carbon numbers 1-6, or the hydroxy low-grade alkyl group of carbon numbers 1-6 among a formula, respectively.)

[Claim 16] The cleaning agent according to claim 15 the fourth class ammonium of whose shown by the general formula [5] is tetramethylammonium hydroxide or hydroxylation trimethyl-2-hydroxyethyl ammonium.

[Claim 17] The cleaning agent according to claim 13 which is that ammonia, primary amine, the second class amine, or the third class amine is indicated to be by the following general formula [4].

[Formula 14]

(R11, R12, and R13 show independently a hydrogen atom, a low-grade alkyl group, or a hydroxy low-grade alkyl group among a formula, respectively.)

[Claim 18] The washing approach on the front face of a semi-conductor characterized by processing the semi-conductor front face where copper wiring was given to the front face with a cleaning agent given in any of claims 1-17 they are that copper wiring was given to the front face.

[Claim 19] The washing approach on the front face of a semi-conductor characterized by giving the semi-conductor front face where copper wiring was given to the front face to a physical washing process under existence of a cleaning agent given in any of claims 1-17 them are.

[Claim 20] The semi-conductor with which copper wiring was given to the front face obtained by washing the semi-conductor front face where copper wiring was given to the front face by the approach according to claim 18 or 19.

[Claim 21] The compound shown by the following general formula [2'] [** 15]

R1 and R2 show independently a hydrogen atom, a hydroxyl group, an alkyl group, or a hydroxyalkyl radical among [type, respectively, r and s show 0 or a positive integer independently, respectively, and R5' shows the radical shown by a hydrogen atom, the hydroxyl group, the alkyl group, the hydroxyalkyl radical, or the following general formula [3'].

[Formula 16]

(R3 and R4 show independently a hydrogen atom, a hydroxyl group, an alkyl group, or a hydroxyalkyl radical among a formula, respectively, and r' and s' show 0 or a positive integer independently, respectively.)

However, r, s, r', and s' remove the case of 0 to coincidence.] The semi-conductor substrate cleaning agent which comes to contain a nitrogen-containing alkalinity compound.

[Claim 22] The cleaning agent according to claim 21 which is the compound in which the compound shown by the general formula [2'] is shown by the following general formula [2''].

[Formula 17]

(R1, R2, R3, R4, r, r', s, and s' is the same as the above among a formula.)

[Claim 23] The cleaning agent according to claim 22 R1 and whose R3 are methyl groups in a general formula [2"] and R2 and whose R4 are isobutyl radicals.

[Claim 24] The cleaning agent according to claim 22 or 23 whose totals of r, r', s, and s' are 1-20 in a general formula [2"].

[Claim 25] The cleaning agent according to claim 22 or 23 whose totals of r, r', s, and s' are 1-18 in a general formula [2"].

[Claim 26] The cleaning agent according to claim 22 which is that as which the compound shown by the general formula [2"] is chosen from the compound shown by the following general formula [6], [7], or [8].

[Formula 18]

(p+p' is 1-20 among a formula.)

[Formula 19]

(p+q+p'+q' is 1-20 among a formula.)

[Formula 20]

(q+q' is 1-20 among a formula.)

[Claim 27] The cleaning agent given in any of claims 21-26 they are chosen from the fourth class ammonium in which a nitrogen-containing alkalinity compound is shown by ammonia, primary amine, the second class amine, the third class amine, or the

following general formula [5].

[Formula 21]

(R6-R9 show among a formula the hydrocarbon residue which may have the hydroxyl group independently, respectively, and M- shows an anion.)

[Claim 28] A cleaning agent given in any of claims 21-26 which are the fourth class ammonium in which a nitrogen-containing alkalinity compound is shown by the general formula [5] they are.

[Claim 29] The cleaning agent according to claim 28 which is that the fourth class ammonium shown by the general formula [5] is indicated to be by the following general formula [5'].

[Formula 22]

(R6-R9 show independently the low-grade alkyl group of carbon numbers 1-6, or the hydroxy low-grade alkyl group of carbon numbers 1-6 among a formula, respectively.)

[Claim 30] The cleaning agent according to claim 28 or 29 whose hydrocarbon residue shown by R5-R6 in a general formula [5] or [5'] is an alkyl group.

[Claim 31] The cleaning agent according to claim 30 whose alkyl group shown by R5-R6 is a methyl group.

[Claim 32] The cleaning agent according to claim 29 the fourth class ammonium of whose shown by the general formula [5'] is tetramethylammonium hydroxide or hydroxylation trimethyl-2-hydroxyethyl ammonium.

[Claim 33] A cleaning agent given in any of claims 21-32 whose semi-conductor substrates are semi-conductor substrates with which copper wiring was given to the front face they are.

[Claim 34] The semi-conductor substrate washing approach characterized by processing a semi-conductor front face with a cleaning agent given in any of claims 21-32 they are.

[Claim 35] The washing approach according to claim 34 that a semi-conductor substrate is a semi-conductor substrate with which copper wiring was given to the front face.

[Claim 36] The semi-conductor substrate obtained by washing a semi-conductor front

face by the approach according to claim 34 or 35.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the cleaning agent and the washing approach on a semi-conductor front face and the front face of a semi-conductor where copper wiring was especially given to the front face.

[0002]

[Description of the Prior Art] In recent years, detailed-ization is progressing with high integration and the structure of LSI is the multilayer structure which metal wiring etc. put on the semi-conductor front face in many steps. Moreover, modification in copper with more low electric resistance (Cu) from the aluminum of the former [wiring / which is used] is proposed.

[0003] The so-called chemical physical polish technique (Cu-CMP) which grinds and carries out flattening of the semi-conductor substrate physically is used for the process which manufactures the semi-conductor which has the multilayer structure by which copper wiring was continued and given to the multilayer on the front face, oxidizing Metal Cu.

[0004] On the other hand, the insulator layer (silicon oxide) which isolates Cu wiring and each Cu wiring is in the unreserved condition, and the wafer front face after a Cu-CMP process is polluted by a lot of impurity metals and particle by the semi-conductor front face after a Cu-CMP process. Cu impurity metal contamination is shaved [Cu] by CMP originates in adsorbing on an insulator layer and remaining as oxidation copper, and particle contamination originates in the slurry used at a CMP process for polish.

[0005] Thus, if copper oxide remains on an insulator layer, a copper element is spread in an insulator layer in heat treatment at a back process, the property of a device deteriorates because insulation falls, and a device will be destroyed in order for isolated wiring to raise connection, i.e., short-circuit, when contamination is remarkable. Therefore, before progressing to degree process, it is necessary to remove copper oxide. Moreover, in order for particle contamination to have a bad influence on degree process similarly, it is necessary to remove as much as possible.

[0006] In order to remove the above-mentioned **** impurity and particle by the above reason, the washing process after a Cu-CMP process is indispensable.

[0007] In the washing process after a Cu-CMP process, if the acid penetrant removers (a

hydrochloric acid, fluoric acid, etc.) usually used as a penetrant remover for semi-conductors are used conventionally, in order to dissolve not only copper oxide but the metal copper of wiring which adhered on the insulator layer and to cause corrosion and an open circuit of wiring, use of the acid penetrant remover concerned is not desirable. Furthermore, when an acid solution is used, a semi-conductor front face and particle pay well electrostatic, and the problem of particle being not only unremovable, but causing reverse adsorption also has them. Moreover, although the alkaline penetrant remover which a semi-conductor front face and particle **** for removal of particle mutually electrostatic is generally confirmed, when penetrant removers which contained the metal ion as a source of alkali, such as a sodium hydroxide and a potassium hydroxide, are used, these metals will stick to an insulator layer (silicon oxide) front face, and an insulating property will be degraded. Moreover, copper solvent power cannot use strongly the penetrant remover of the inorganic alkali (aqueous ammonia etc.) which does not contain a metal ion among alkaline penetrant removers.

[0008] On the other hand, although the penetrant remover containing the fourth class ammonium does not corrode copper wiring and has the advantage that the removal effectiveness of particle is also high, since the fourth class ammonium is strong-base nature, it has the fault of the etching force over an insulator layer being strong, and damaging the front face which carried out flattening at the CMP process. In order to cancel such a fault, by adding a hydrogen peroxide to the fourth class ammonium, it is known that it is possible to make an etch rate late. However, in this case, by the oxidizing power of a hydrogen peroxide, the front face of copper wiring oxidizes and the problem that conductivity will worsen arises.

[0009] Thus, the penetrant remover which can remove a surface impurity did not exist until now, without having not caused the corrosion or oxidation of copper wiring for the semi-conductor substrate which gave copper wiring, and starting a surface dry area.

[0010]

[Problem(s) to be Solved by the Invention] This invention offers the cleaning agent and the washing approach of removing the impurity of the front face concerned effectively, without not having been made in view of the above-mentioned **** situation, and not causing the corrosion or oxidation of copper wiring for a semi-conductor front face and the semi-conductor front face where copper wiring was especially given to the front face, and starting a surface dry area.

[0011]

[Means for Solving the Problem] This invention consists of the following configurations.

[0012] (1) The cleaning agent for semi-conductor front faces with which copper wiring

was given to the front face which comes to contain a nonionic surfactant.

[0013] (2) The washing approach on the front face of a semi-conductor characterized by processing the semi-conductor front face where copper wiring was given to the front face with the cleaning agent which comes to contain a nonionic surfactant that copper wiring was given to the front face.

[0014] (3) The semi-conductor which was obtained by processing the semi-conductor front face where copper wiring was given to the front face with the cleaning agent which comes to contain a nonionic surfactant and with which copper wiring was given to the front face.

[0015] As a result of repeating research wholeheartedly that this invention person etc. should attain the above-mentioned purpose, by washing the semi-conductor front face where copper wiring was given using the cleaning agent containing a nonionic surfactant The oxidation copper which is adsorbing on an insulator layer or copper wiring, and an impurity like particle can be removed effectively, without being able to control the etch rate of an insulator layer, and not causing the corrosion or oxidation of copper wiring, and starting a surface dry area, Furthermore, such effectiveness is [0016] in the molecule as a nonionic surfactant.

[Formula 23]

[0017] When especially the thing that comes out and has the acetylenic group shown used the fourth class ammonium together in a desirable thing list also especially in such a surfactant and nitrogen-containing alkalinity compounds, such as ammonia, the first class, the third class amine, or the fourth class ammonium, based on a header and discovery of these single strings, it came to complete this invention for the effectiveness being promoted further.

[0018] Although each thing known conventionally is used as a nonionic surfactant in this invention, it is [0019] in the molecule.

[Formula 24]

[0020] What comes out and has the radical (acetylenic group) shown is desirable, and it is [0021] especially in a molecule.

[Formula 25]

[0022] What comes out and has the radical (acetylenic group) shown and a polyoxyalkylene group is desirable.

[0023] As the polyoxyalkylene group concerned, what is shown, for example by the following general formula [1] is mentioned.

[0024]

[Formula 26]

[0025] (X shows an alkylene group among a formula and y shows a positive integer) .

[0026] as the alkylene group shown by X in a general formula [1] — the low-grade alkylene group of the shape of a straight chain, the shape of branching, and the annular carbon numbers 1-6 — desirable — for example, a methylene group and ethylene, a propylene radical, a butylene radical, a methyl methylene group, ethyl ethylene, a methyl ethylene radical, a methyl propylene radical, an ethyl propylene radical, and a pentene radical — it passes, a xylene radical etc. is mentioned to a xylene radical a cyclo pentene radical, and cyclo, and ethylene or especially a propylene radical is desirable especially. Moreover, since a positive integer is shown, it is 1-8 preferably, foaming is usually suppressed also when the thing of 2-8 has low cellularity and y uses together with physical washing especially, 1-10, and, and it is hard to generate a trouble with a bubble, y is especially desirable. In addition, all of y oxy-alkylene groups may be the same, and they may consist of two sorts or more than it. In the oxy-alkylene group shown by $-(X-O)-$ in a general formula [1], an oxyethylene radical, an oxypropylene radical, etc. are desirable, for example, and what consists only of an oxyethylene radical, for example, the thing which consists only of an oxypropylene radical, especially the thing that consists of combination of an oxyethylene radical and an oxypropylene radical are desirable as a polyoxyalkylene group shown by $-(X-O)_y-$. In addition, when it is what consists of combination of an oxyethylene radical and an oxypropylene radical, the oxyethylene radical of both ratio is usually 70% or more preferably 50% or more.

[0027] It is [0028] in the above-mentioned **** and a molecule.

[Formula 27]

[0029] As an example of a nonionic surfactant of coming out and having the radical shown and the polyoxyalkylene group shown by said general formula [1], what is shown, for example by the following general formula [2] is mentioned.

[0030]

[Formula 28]

[0031] X1 shows a low-grade alkylene group among [type, n shows a positive integer, R1 and R2 show independently a hydrogen atom, a hydroxyl group, an alkyl group, or a hydroxyalkyl radical, respectively, and R5 shows the radical shown by a hydrogen atom, the hydroxyl group, the alkyl group, the hydroxyalkyl radical, or the following general formula [3].

[0032]

[Formula 29]

[0033] (R3 and R4 show independently a hydrogen atom, a hydroxyl group, an alkyl group, or a hydroxyalkyl radical among a formula, respectively, X2 shows a low-grade alkylene group, and m shows a positive integer.)]

[0034] The low-grade alkylene group shown by X1 and X2 in the above-mentioned general formula [2] and [3] is the same as X in the **** general formula [1] mentioned above. Moreover, m and n are the same as y in the **** general formula [1] similarly mentioned above. In addition, when R5 in a general formula [2] is a general formula [3], it is 2-16 preferably, and since foaming is suppressed especially also when the thing of 4-16 has low cellularity and uses together with physical washing, 2-20, and, and it is hard to generate a trouble with a bubble, it is usually especially desirable [the sum total of m and n].

[0035] Also in the nonionic surface active agent shown by the above-mentioned **** general formula [2], that X1 and whose X2 are ethylene or/and a propylene radical is desirable. As these desirable things, what is shown, for example by the following general formula [2'] is mentioned.

[0036]

[Formula 30]

[0037] R1 and R2 are the same as the above among [type, r and s show 0 or a positive integer independently, respectively, and R5' shows the radical shown by a hydrogen atom, the hydroxyl group, the alkyl group, the hydroxyalkyl radical, or the following general formula [3'].

[0038]

[Formula 31]

[0039] (R3 and R4 are the same as the above among a formula, and r' and s' show 0 or a positive integer independently, respectively.) However, r, s, r', and s' remove the case of 0 to coincidence.]

[0040] Especially the thing whose radical shown by R5' in a general formula [2'] is a general formula [3'] especially, i.e., the thing shown by the following general formula [2''], is desirable.

[0041]

[Formula 32]

[0042] (a formula — inside — R — one — R — two — R — three — R — four — R — five — r — r — ' — s — and — s — ' — the above — being the same .)

[0043] In addition, it sets to the above-mentioned general formula [2'] and [2''], and is [0044].

[Formula 33]

[0045] The thing (the so-called block copolymer) and oxyethylene radical, and oxypropylene radical which consist of **, r blocks of an oxyethylene radical, and s blocks of an oxypropylene radical join together in random order, and the former total

means that (the so-called random copolymer) whose latter total is s pieces by r pieces.
Moreover, the above-mentioned general formula [3'] and [0046] in [2"]
[Formula 34]

[0047] It is the same as that of **.

[0048] the nonionic surfactant concerning this invention — the very thing — it can prepare easily by the well-known approach. Namely, the glycol compound shown in U.S. Pat. No. 3291607 by the following general formula [2-1] according to the approach of a publication in order to, prepare the compound whose radical shown by R5 in a general formula [2] is a general formula [3] for example, and [0049]
[Formula 35]

[0050] (R1-R4 are the same as the above among a formula.) What is necessary is just to make the following general formula [2-2] or/and the alkylene oxide corresponding to [3-1] react.

[0051]

[Formula 36]

[0052] And [0053]

[Formula 37]

[0054] (X1, X2, n, and m are the same as the above among a formula.)

[0055] as the alkyl group shown by R1-R5, and R5' in the above-mentioned formula [2], [3], [2'], [3'], and [2"] — saturation — partial saturation — ***** — the shape of a straight chain, the shape of branching, and the annular carbon numbers 1-10 — desirable — 1-6 — it is 1-3 still more preferably. Specifically For example, a methyl group, an ethyl group, n-propyl group, n-butyl, n-pentyl radical, n-hexyl group, n-octyl radical, n-nonyl radical, Saturation straight chain alkyl groups, for example, iso-propyl groups, such as n-deca nil radical, iso-butyl, sec-butyl, tert-butyl, an iso-pentyl radical, A

sec-pentyl radical, a tert-pentyl radical, a neopentyl radical, an iso-hexyl group, Saturation branching alkyl groups, such as a sec-hexyl group and a tert-hexyl group, For example, annular alkyl groups, for example, a vinyl group, such as a cyclopentyl group and a cyclohexyl radical, Partial saturation branching alkyl groups, such as partial saturation straight chain alkyl groups, for example, an iso-propenyl radical, such as n-propenyl radical and n-butenyl group, an iso-butenyl group, a sec-butenyl group, and a tert-butenyl group, are mentioned. As a hydroxyalkyl radical, 1-3, the thing by which only the hydrogen atom of the end was more preferably permuted with the hydroxyl group are preferably mentioned 1 or more than it among the hydrogen atoms of the arbitration of these alkyl groups.

[0056] In addition, it is 1-16 preferably, and since cellularity is low, foaming is suppressed also when it uses together with physical washing, 1-20, and, and it is hard to generate a trouble with a bubble, especially the thing of 4-16 is usually especially desirable [the sum total of r, s, r' and s']. The thing whose s and s' is 0-2 independently, respectively and whose r and r' is 4-6 independently especially, respectively is more desirable.

[0057] As an example of a nonionic surface active agent of having an acetylenic group in a molecule, it is the diisobutyl dimethyl butynediol polyoxy-ethylene-glycol ether (1, 4-diisobutyl-1, 4-dimethylbut-2-yn diol polyoxyethylene glycol ether) in this invention shown, for example by the following general formula [6].

[0058]

[Formula 38]

[0059] the inside of [type, and the total (p+p') of p and p' — usually — 1-20 — desirable — 1-16 — it is 4-16 more preferably.] [0060] For example, the diisobutyl dimethyl butynediol polyoxyethylene / polyoxypropylene glycol ether shown by the following general formula [7] (1, 4-diisobutyl-1, 4-dimethylbut-2-yn diol polyoxyethylene-polyoxypropylene glycol ether)

[0061]

[Formula 39]

[0062] the inside of [type, and the total ($p+q+p'+q'$) of p , q , p' , and q' — usually — 1-20 — desirable — 1-16 — it is 4-16 more preferably.] [0063] For example, diisobutyl dimethyl butynediol polyoxypropylene glycol ether shown by the following general formula [8] (1, 4-diisobutyl-1, 4-dimethylbut-2-yn diol polyoxypropylene glycol ether)

[0064]

[Formula 40]

[0065] the inside of [type, and the total ($q+q'$) of q and q' — usually — 1-20 — desirable — 1-16 — it is 4-16 more preferably.] ** is mentioned.

[0066] The thing or commercial item prepared by the **** approach mentioned above, or any is sufficient as the nonionic surfactant used in this invention. The above-mentioned **** nonionic surfactant may be used independently, or two or more sorts, it may combine suitably and it may be used.

[0067] That the amount of the nonionic surface active agent used should just be more than critical micelle concentration, if thinner than it, the rate of etching will become quick and effectiveness will fade. Although there is no ***** generally as the concrete amount used since it changes with classes of surfactant, it is usually 1 ppm or more, and there is especially no upper limit, for example. However, when economical efficiency etc. is taken into consideration, 1-10000 ppm is desirable and is 10-1000 ppm more preferably.

[0068] As the ammonia in this invention, the first class, or the third class amine, what is shown, for example by the following general formula [4] is mentioned.

[0069]

[Formula 41]

[0070] (R11, R12, and R13 show independently a hydrogen atom, a low-grade alkyl group, or a hydroxy low-grade alkyl group among a formula, respectively.)

[0071] As a low-grade alkyl group shown by R11-R13 in a general formula [4] The thing of the shape of a straight chain, the shape of branching, and the annular carbon numbers 1-6 is mentioned. For example, specifically For example, a methyl group, an ethyl group, n-propyl group, an iso-propyl group, n-butyl, iso-butyl, sec-butyl, tert-butyl, n-pentyl radical, an iso-pentyl radical, a sec-pentyl radical, a tert-pentyl radical, a neopentyl radical, n-hexyl group, an iso-hexyl group, a sec-hexyl group, a tert-hexyl group, a cyclopentyl group, a cyclohexyl radical, etc. are mentioned. As a hydroxy low-grade alkyl group shown by R11-R13 in a general formula [4] That by which the hydrogen atom of the end was preferably permuted with the hydroxyl group is mentioned 1 or more than it among the hydrogen atoms of the arbitration of the above-mentioned **** low-grade alkyl group. Specifically For example, a hydroxymethyl group, hydroxyethyl radical, 3-hydroxy-n-propyl group, 4-hydroxy-n-butyl, 1-methyl-2-hydroxyethyl radical, 2-methyl-3-hydroxypropyl radical, 1, and 1-dimethyl-2-hydroxyethyl radical etc. is mentioned.

[0072] As an example of the compound shown by the general formula [4], for example, ammonia, For example, primary amine, such as monomethylamine, ethylamine, n propylamine, and n butylamine, For example, dimethylamine, diethylamine, a methylethyl amine, G n propylamine, The second class amines, for example, a trimethylamine, such as G n butylamine, triethylamine, The third class amines, such as methyl diethylamine, tree n propylamine, and tree n butylamine, For example, third class hydroxy amines, such as second class hydroxy amines, for example, triethanolamine etc., such as first-class hydroxy amines, for example, diethanolamine etc., such as monoethanolamine, etc. are mentioned.

[0073] As the fourth class ammonium in this invention, what is shown, for example by the following general formula [5] is mentioned.

[0074]

[Formula 42]

[0075] (R6-R9 show among a formula the hydrocarbon residue which may have the hydroxyl group independently, respectively, and M- shows an anion.)

[0076] As hydrocarbon residue of the hydrocarbon residue which may have the

hydroxyl group shown by R6-R9 in a general formula [5], any of aliphatic series, aromatic series, aroma aliphatic series, or an alicycle group are sufficient, and as aliphatic series in aliphatic series and aroma aliphatic series, it may be [being saturation] unsaturated, or the shape of the shape of a straight chain and branching has. As a typical thing of these, the alkyl group of the shape of a straight chain, the shape of branching, annular saturation, or partial saturation, an aralkyl radical, an aryl group, etc. are mentioned, for example. As an alkyl group, the low-grade alkyl group of 1-6, especially the low-grade alkyl group of carbon numbers 1-4 usually have a desirable carbon number. Specifically For example, a methyl group, an ethyl group, n-propyl group, an iso-propyl group, n-butyl, iso-butyl, sec-butyl, tert-butyl, n-pentyl radical, an iso-pentyl radical, a sec-pentyl radical, a tert-pentyl radical, A neopentyl radical, n-hexyl group, an iso-hexyl group, a sec-hexyl group, A tert-hexyl group, a cyclopentyl group, a cyclohexyl radical, a vinyl group, n-propenyl radical, an iso-propenyl radical, n-butenyl group, an iso-butenyl group, a sec-butenyl group, a tert-butenyl group, etc. are mentioned. As an aralkyl radical, the thing of carbon numbers 7-12 is usually mentioned, and, specifically, benzyl, a phenethyl radical, a phenylpropyl radical, phenyl butyl, a phenyl hexyl group, a methylbenzyl radical, a methyl phenethyl radical, ethyl benzyl, etc. are mentioned. As an aryl group, the thing of carbon numbers 6-14 is usually mentioned, a phenyl group, o-tolyl group, m-tolyl group, p-tolyl group, 2, 3-xylyl group, 2, 4-xylyl group, 2, 5-xylyl group, 2, 6-xylyl group, 3, 5-xylyl group, a naphthyl group, an anthryl radical, etc. specifically mention, and it is ****. In addition, in the ring of the above-mentioned **** aryl group or an aralkyl radical, you may have low-grade alkyl groups, such as a methyl group and an ethyl group, a halogen atom, a nitro group, the amino group, etc. as a substituent. That by which the above-mentioned hydrogen atom of hydrocarbon residue was permuted with the hydroxyl group as hydrocarbon residue which has a hydroxyl group is mentioned. As an anion shown by M- in a general formula [5], OH- etc. is mentioned, for example.

[0077] As an example of the above-mentioned fourth class ammonium of ****, the following are mentioned, for example. Tetramethylammonium hydroxide (TMAH), hydroxylation trimethyl-2-hydroxyethyl ammonium (choline), Hydroxylation tetraethylammonium, hydroxylation tetrapropylammonium, Hydroxylation tetrabutylammonium, hydroxylation monomethyl triethyl ammonium, Hydroxylation dimethyl diethyl ammonium, hydroxylation trimethyl monoethyl ammonium, Hydroxylation monomethyl TORIPURO pill ammonium, hydroxylation dimethyl dipropyl ammonium, Hydroxylation trimethyl monopropyl ammonium, hydroxylation monomethyl tributyl ammonium, Hydroxylation dimethyl dibutyl ammonium,

hydroxylation trimethyl monobutyl ammonium, Hydroxylation monoethyl TORIPURO pill ammonium, hydroxylation diethyl dipropyl ammonium, Hydroxylation triethyl monopropyl ammonium, hydroxylation monoethyl tributyl ammonium, Hydroxylation diethyl dibutyl ammonium, hydroxylation triethyl monobutyl ammonium, Hydroxylation monopropyl tributyl ammonium, hydroxylation dipropyl dibutyl ammonium, Hydroxylation TORIPURO pill monobutyl ammonium, hydroxylation triethyl-2-hydroxyethyl ammonium, Hydroxylation TORIPUROPIRU-2-hydroxyethyl ammonium, hydroxylation tributyl-2-hydroxyethyl ammonium, Hydroxylation trimethyl-3-hydroxypropyl ammonium, hydroxylation triethyl-3-hydroxypropyl ammonium, Hydroxylation TORIPUROPIRU-3-hydroxypropyl ammonium, hydroxylation tributyl-3-hydroxypropyl ammonium, Hydroxylation trimethyl-4-hydroxy butyl ammonium, hydroxylation triethyl-4-hydroxy butyl ammonium, Hydroxylation TORIPUROPIRU-4-hydroxy butyl ammonium, hydroxylation tributyl-4-hydroxy butyl ammonium, Hydroxylation trimethyl-3-hydroxy butyl ammonium, hydroxylation triethyl-3-hydroxy butyl ammonium, Hydroxylation TORIPUROPIRU-3-hydroxy butyl ammonium, hydroxylation tributyl-3-hydroxy butyl ammonium, Hydroxylation dimethyl ethyl-2-hydroxyethyl ammonium, hydroxylation methyl diethyl-2-hydroxyethyl ammonium, Hydroxylation dimethyl ethyl-3-hydroxypropyl ammonium, hydroxylation methyl diethyl-3-hydroxypropyl ammonium, Hydroxylation dimethyl ethyl-4-hydroxy butyl ammonium, hydroxylation methyl diethyl-4-hydroxy butyl ammonium, Hydroxylation dimethyl ethyl-3-hydroxy butyl ammonium, hydroxylation methyl diethyl-3-hydroxy butyl ammonium, Hydroxylation JIMECHIRUJI (2-hydroxyethyl) ammonium, hydroxylation JIMECHIRUJI (3-hydroxypropyl) ammonium, Hydroxylation JIMECHIRUJI (3-hydroxy butyl) ammonium, hydroxylation JIMECHIRUJI (4-hydroxy butyl) ammonium, Hydroxylation JIECHIRUJI (2-hydroxyethyl) ammonium, hydroxylation JIECHIRUJI (3-hydroxypropyl) ammonium, Hydroxylation JIECHIRUJI (3-hydroxy butyl) ammonium, hydroxylation JIECHIRUJI (4-hydroxy butyl) ammonium, Hydroxylation methyl ECHIRUJI (2-hydroxyethyl) ammonium, hydroxylation methyl ECHIRUJI (3-hydroxypropyl) ammonium, Hydroxylation JIECHIRUJI (3-hydroxy butyl) ammonium, hydroxylation methyl ECHIRUJI (4-hydroxy butyl) ammonium, Hydroxylation MECHIRUTORI (2-hydroxyethyl) ammonium, hydroxylation ECHIRUTORI (2-hydroxyethyl) ammonium, Hydroxylation pro PIRUTORI (2-hydroxyethyl) ammonium, hydroxylation BUCHIRUTORI (2-hydroxyethyl) ammonium, Hydroxylation MECHIRUTORI (3-hydroxypropyl) ammonium, hydroxylation ECHIRUTORI (3-hydroxy butyl) ammonium, Hydroxylation

MECHIRUTORI (4-hydroxy butyl) ammonium, hydroxylation ECHIRUTORI (4-hydroxy butyl) ammonium, hydroxylation MECHIRUTORI (3-hydroxy butyl) ammonium, hydroxylation ECHIRUTORI (3-hydroxy butyl) ammonium. Also in these, tetramethylammonium hydroxide (TMAH), especially hydroxylation trimethyl-2-hydroxyethyl ammonium (choline), etc. are desirable.

[0078] The fourth class ammonium shown by the compound shown by the above-mentioned general formula [4] or the general formula [5] may be used independently, or two or more sorts, it may combine suitably and it may be used.

[0079] Since the amount of the fourth class ammonium used shown by the compound shown by the general formula [4] used in this invention or the general formula [5] changes with classes, it does not generally have *****, but since the rate of etching becomes slow by low concentration not much and effectiveness fades, it is usually more than 0.003% (w/v), for example. Moreover, although there is especially no upper limit, when economical efficiency etc. is taken into consideration, 0.003 - 10% (w/v) is desirable, and is 0.05 - 1% (w/v) still more preferably 0.01 to 6% (w/v) more preferably.

[0080] (1) As a desirable mode of the cleaning agent of this invention, the following are mentioned, for example.

(a) The fourth class ammonium shown as a nitrogen-containing alkalinity compound by the ammonia shown by the general formula [4], the first class, the third class amine, or the general formula [5], and [0081]

[Formula 43]

[0082] (— R6, R7, R8, R9, R11, R12, R13, and M— are the same as the above among a formula.) — the nonionic surfactant shown by the (b) general formula [2] — 0083]

[Formula 44]

[0084] (— R1, R2, R5, X1, and n are the same as the above among a formula.) — cleaning agent for semi-conductors which becomes as a major component.

[0085] (2) as the more desirable mode of the cleaning agent of this invention — a less or equal — like — come out.

(a') The fourth class ammonium shown by the general formula [5], and [0086]
[Formula 45]

[0087] (— R6, R7, R8, R9, and M— are the same as the above among a formula. D) — the nonionic surfactant shown by the general formula (b') [2'] — 0088]
[Formula 46]

[0089] (— R1, R2, R5', and r and s are the same as the above among a formula.) — cleaning agent for semi-conductors which becomes as a major component.

[0090] (3) as the still more desirable mode of the cleaning agent of this invention — a less or equal — like — come out.

(a'') The fourth class ammonium shown by the general formula [5'], and [0091]
[Formula 47]

[0092] (— R6, R7, R8, and R9 are the same as the above among a formula. D) — the nonionic surfactant shown by the general formula (b'') [2''] — 0093]
[Formula 48]

[0094] (— a formula — inside — R — one — R — two — R — three — R — four — r — s — r — ' — and — s — ' — the above — being the same .) — cleaning agent for semi-conductors which becomes as a major component.

[0095] In addition, in the above-mentioned mode, especially the case where a methyl group, and R2 and R4 are [R1 and R3 in a general formula [2'']] isobutyl radicals, and all of R6-R9 in a general formula [5'] are methyl groups, or three are a methyl group among those, and the one remaining is 2-hydroxyethyl radical is desirable.

[0096] Although the cleaning agent of this invention can be used also as cleaning agents, such as not only a semi-conductor but a printed circuit board, and a LCD substrate, especially the above-mentioned **** mode is useful to washing on the front face of a semi-conductor where copper wiring was given to the front face.

[0097] The cleaning agent of this invention is usually in the condition of a water solution, and is prepared by making water carry out the addition dissolution of the above-mentioned **** nonionic surfactant or a nonionic surfactant, and the nitrogen-containing alkalinity compound.

[0098] Thus, as for the prepared cleaning agent of this invention, it is desirable to perform filtration processing etc. before use. Moreover, although the water used here should just be refined by distillation, ion exchange treatment, etc., its so-called ultrapure water used in this field is more desirable.

[0099] the cleaning agent of this invention — alkalinity — desirable — usually — nine or more pH — desirable — pH 9-12 — it is pH 9.5-10.5 more preferably. Since a possibility of etching SiO₂ which is an interlayer insulation film decreases more and electric repulsion with a semi-conductor front face and particle becomes large further by considering as such pH range, particle and the cleaning effect of CuO improve.

[0100] In order to consider as the **** pH range which described the cleaning agent of this invention above, as long as it requires, carboxylic acids, such as pH regulator usually used in this field, for example, a citric acid, oxalic acid, a phthalic acid, and a tartaric acid, these derivatives or these salts, a phosphoric acid, a phosphoric-acid derivative, or a salt may be used.

[0101] Moreover, the cleaning agent of this invention has especially the desirable thing that has buffer capacity in above-mentioned **** pH within the limits. independent in what has buffer capacity by **** pH within the limits which itself described above among the above-mentioned **** pH modifiers, in order to give buffer capacity to the cleaning agent of this invention — or, even if it combines two or more sorts Or although you may use combining pH regulators other than this and it does not have buffer capacity in itself The thing which can give buffer capacity to the cleaning agent of this invention, or the thing which can give buffer capacity to the cleaning agent of this invention by using it combining a nitrogen-containing alkalinity compound may be used by using two or more sorts, combining. In addition, especially when only the above-mentioned **** nitrogen-containing alkalinity compound can give buffer capacity to the cleaning agent of this invention, it cannot be overemphasized that it is not necessary to use pH regulator.

[0102] Since it changes as amount of these pH regulator used with classes of pH

regulator to be used, there is no ***** generally, but when the cleaning agent of this invention is made to add, it is 0.0001 - 10% (w/v) usually [of the cleaning agent whole quantity] 0.001 - 1% (w/v) preferably that what is necessary is just the amount which becomes **** pH within the limits which the cleaning agent concerned described above. [0103] Moreover, in the cleaning agent of this invention, the chelating agent which does not have the capacity to dissolve copper wiring may be added. By adding such a chelating agent, the copper oxide distributed in liquid can be solubilized, and re-adsorption can be suppressed, and Fe, aluminum, etc. which are the impurity of the slurry origin at a CMP process can also be removed from a front face. as the chelating agent which does not have the capacity to dissolve such copper wiring — ethylenediaminetetraacetic acid (EDTA), trans-1, and 2-diamino cyclohexane - N, N, N', and N' — phosphonic acid, such as carboxylic acids (methylene phosphonic acid) (EDTPO), for example, ethylenediamine tetrakis etc., such as -4 acetic acid (CyDTA) and nitrilotriacetic acid (NTA), is mentioned. Since it changes as amount of these chelating agents used with classes of chelating agent to be used, there is no ***** generally, but when the cleaning agent of this invention is made to add, it is 0.0001 - 1% (w/v) usually [of the cleaning agent whole quantity] 0.001 - 0.1% (w/v) preferably that what is necessary is just the amount which can do so the **** effectiveness which the cleaning agent concerned described above.

[0104] furthermore, the purpose which suppresses separation with the above-mentioned **** nonionic surfactant and the above-mentioned nitrogen-containing alkalinity compound in the cleaning agent of this invention — small quantity — for example, 0.1 - 1% (w/v) of organic solvent may usually be added preferably 0.01 to 5% (w/v). As an organic solvent, a methanol, ethanol, isopropyl alcohol, an acetone, etc. are mentioned, for example.

[0105] Into the cleaning agent of this invention, the reagents usually used in this field in addition to the above-mentioned **** nonionic surfactant, a nitrogen-containing alkalinity compound, pH regulator, a chelating agent, and an organic solvent can be used. Such reagents protect Cu of wiring, and are used in order to prevent the corrosion of Cu. For example, reducing agents, such as a hydrazine or its derivative, an ascorbic acid, formic acid, and formalin, For example, metallic corrosion inhibitors, such as benzotriazol or its derivative, and thiourea etc., Improve the wettability of a cleaning agent to a semi-conductor front face, and are used in order to raise a cleaning effect. They are surface active agents other than a nonionic surface active agent (for example, amphoteric surface active agents, such as cation system surface active agents, such as anion system surface active agents, such as dodecylbenzenesulfonic acid, and alkyl

trimethylammonium, and carboxy betaine etc.) etc.

[0106] What is necessary is just to use these reagents by the density range usually used in this field. For example, the amount of the reducing agent used is usually 0.05 - 1 % of the weight preferably 0.01 to 5% of the weight that what is necessary is just the amount which can prevent oxidation of Metal Cu. Moreover, it is 0.05 - 1 % of the weight preferably, and the amount of surfactants used other than a nonionic surfactant is [that what is necessary is just the amount which the amount of the metallic corrosion inhibitor used forms Metal Cu and weak coupling, and can control the solvent power of the cleaning agent to Cu] usually 0.001 - 0.1 % of the weight preferably 0.0001 to 1% of the weight 0.01 to 5% of the weight that what is necessary is just the amount in which the surface tension of a cleaning agent may be reduced.

[0107] What is necessary is just to process the washing approach of this invention with the cleaning agent of **** this invention which described above the semi-conductor front face where Cu wiring was given to the front face.

[0108] the very thing usually performed in this field as an approach of processing the semi-conductor front face where Cu wiring was given to the front face with the cleaning agent of this invention — specifically, approaches, such as DIP processing only immersed into a cleaning agent in a semi-conductor and sheet processing which sprinkles a cleaning agent over a semi-conductor in the shape of a shower, are mentioned that what is necessary is just the approach of washing a well-known semi-conductor front face.

[0109] Furthermore, in this invention, CuO can be more effectively removed by using physical washing together at the time of washing. Giving the semi-conductor front face where Cu wiring was given to the front face to a physical washing process under existence of the cleaning agent of this invention as the concrete approach of concomitant use etc. is mentioned.

[0110] In the above-mentioned approach, the approach of giving to a physical washing process as a condition in which the cleaning agent of this invention was made to specifically exist by the above-mentioned **** DIP processing, sheet processing, etc. as an approach in which the cleaning agent of this invention is made to exist etc. is mentioned. Moreover, brush scrub washing which washes a semi-conductor front face, for example, using the brush made from polyvinyl alcohol of high-speed rotation etc. as physical washing (process), megasonic washing using a RF, etc. are mentioned.

[0111] As more concrete technique in the case of using physical washing together For example, the method of performing physical washing, after considering as the condition of having taken out the semi-conductor out of the penetrant remover concerned after

being immersed into the cleaning agent of this invention, and having made the cleaning agent concerned existing in a semi-conductor front face, How to perform physical washing while the semi-conductor had been made immersed into the cleaning agent of this invention, The method of performing physical washing etc. is mentioned sprinkling the cleaning agent of this invention over the method of performing physical washing, or a semi-conductor front face, after considering as the condition of having sprinkled the cleaning agent of this invention over the semi-conductor front face, and having made the cleaning agent concerned existing in a semi-conductor front face.

[0112] When the cleaning agent of this invention containing a nonionic surfactant is used, the effectiveness of allowing neither the particle of the slurry origin which protects copper wiring and floats in a penetrant remover, nor the slag of an insulator layer etched slightly to come near is done so. When the cleaning agent of this invention which contains the fourth class ammonium and a nonionic surfactant especially is used, etching of the insulator layer by the fourth class ammonium can be reduced, the advantage of the fourth class ammonium with the high effectiveness of removing particle can be employed efficiently, without corroding copper wiring, therefore etching of an insulator layer is suppressed to the minimum, and a surface dry area is not started. And re-adsorption of the copper oxide which exfoliated is also prevented effectively.

[0113] Moreover, in ionic surfactants, such as cationicity, anionic, or both sexes, it may combine with a semi-conductor front face electrically, and washing may be barred, or the surface charge of the particle of the slurry origin which originally considers electric repulsion as a semi-conductor front face with alkalinity may be changed, and re-adsorption of particle may be caused.

[0114] As mentioned above, a nonionic surface active agent, especially the nonionic surface active agent which has an acetylenic group in a molecule, With this, furthermore, by for example, nitrogen-containing alkalinity compounds, such as ammonia, the first class, the third class amine, or the fourth class ammonium, and the penetrant remover which contains both of the fourth class ammonium even especially in inside Without not causing the corrosion or oxidation of copper wiring and starting a surface dry area, if the semi-conductor front face which gave copper wiring is washed, the impurity which is sticking to a front face can be removed and the effectiveness that surface cleanliness can be improved is especially done so notably.

[0115] As described above, although the cleaning agent of this invention is very useful to washing on the front face of a semi-conductor where copper wiring was given to the front face, its wiring of those other than copper, such as for example, not only a thing but aluminum wiring with which copper wiring was given, and a tungsten plug, is

usable also in washing on the front face of a semi-conductor given to the front face. Furthermore, the cleaning agent of this invention is applicable not only to a semi-conductor front face but washing of front faces, such as a printed circuit board and a LCD substrate, again.

[0116] Although an example and the example of a comparison are given to below, this invention is not limited at all by these.

[0117] In addition, the nonionic surfactant used in the example below is compoundable with the reaction of the glycol compound and alkylene oxide which correspond to U.S. Pat. No. 3291607 according to the approach of a publication.

[0118] Moreover, the thermal oxidation film wafer and metal contamination wafer which were used in this example and the example of a comparison, A copper deposition wafer, a particle contamination thermal oxidation film wafer, and a particle contamination copper deposition wafer use what was prepared by the following approaches, respectively. Moreover, the amount of adsorption (residual copper concentration) and the number of particle of a copper atom which are carrying out adsorption survival were measured by the following approaches, respectively on the thickness of the oxide film of a thermal oxidation film wafer, the thickness of the copper of a copper deposition wafer front face, and a metal contamination wafer front face.

[0119] [Thermal oxidation film wafer] After processing the 4 inch silicon wafer in the fluoric acid water solution 1% and removing the surface natural oxidation film, it heat-treated at 800 degrees C, and the thing in which the thermal oxidation film (silicon oxide, insulator layer) was formed on the wafer front face was used as the thermal oxidation film wafer. In addition, the thickness of the oxide film of the thermal oxidation film wafer concerned checked that it was 500A by the approach shown below.

[0120] [Metal contamination wafer] After having been immersed in the nitric-acid water solution which added the copper ion for 1 minute so that a thermal oxidation film wafer might be set to 1 ppm, and carrying out style backwashing by water during 10 minutes with ultrapure water, what carried out spin desiccation was used as the metal contamination wafer. In addition, to the metal contamination wafer concerned, it checked that the copper atom was carrying out 3×10^{14} atom / cm² adsorption survival by the approach shown below.

[0121] [Copper deposition wafer] The thing which made metal copper deposit on a thermal oxidation film wafer front face by the sputtering method was used as the copper deposition wafer. In addition, the thickness of the copper of the copper deposition wafer front face concerned checked that it was 1000A by the approach shown below.

[0122] [A particle contamination thermal oxidation film wafer and particle

contamination copper deposition wafer] After being immersed in the alumina slurry water solution for 1 minute 3% with a mean particle diameter of 0.2 micrometers, respectively and carrying out style backwashing by water during 10 minutes of a thermal oxidation film wafer or the copper deposition wafer with ultrapure water, what carried out spin desiccation was used as the particle contamination thermal oxidation film wafer or the particle contamination copper deposition wafer, respectively. In addition, the approach shown below — the particle contamination thermal oxidation film wafer concerned — particle — about 850 pieces / 4 inch wafer, and a particle contamination copper deposition wafer — particle — about 90 pieces / 4 inch wafer — it checked each carrying out adsorption survival.

[0123] [Thickness measurement method of an oxide film] It measured by the thickness gage (ellipsometer).

[0124] [Copper thickness measurement method] The wafer was divided into one half, the cross section was observed with the electron microscope, and copper thickness was measured.

[0125] The [amount (residual copper concentration) measuring method of copper atomic adsorption] On the wafer front face, after carrying out dissolution recovery of the copper which carried out adsorption survival in a fluoric acid-nitric-acid water solution, the copper concentration in this recovery liquid was measured with the atomic absorption method (graphite furnace atomic-absorption-analysis equipment). Based on the obtained measured value, the amount of adsorption (residual copper concentration) of a copper atom was calculated.

[0126] The [number measuring method of particle] The particle which is carrying out adsorption survival was measured with surface dust-particle-inspection equipment (particle counter) on the wafer front face.

[0127] In addition, in this example and the example of a comparison, all especially of % which expresses concentration as long as there is no notice, and ppm and ppb show a weight ratio. Moreover, all the water to be used was ultrapure water, and it was used after checking that copper was 0.01 or less ppb.

[0128]

[Example] The diisobutyl dimethyl butynediol polyoxy-ethylene-glycol ether whose number of average mols of an oxyethylene radical [p+p'] tetramethylammonium hydroxide (TMAH) is indicated to be 1% in example 1 ultrapure water by the following general formula [6] which is a nonionic surface active agent, and is 10 [0129]

[Formula 49]

[0130] (— it is hereafter written as a surfactant 10.) — 60 degrees C was immersed in the cleaning agent (12 or more pH) which dissolved 0.03% for 10 minutes in the thermal oxidation film wafer produced by the above-mentioned approach. Then, the wafer was pulled up, and after carrying out a rinse for 10 minutes and carrying out spin desiccation with ultrapure water, in order to check the existence of the corrosion of an oxide film, the oxide-film thickness of a thermal oxidation film wafer was measured. A result is collectively shown in Table 1.

[0131] Except having used the cleaning agent (12 or more pH) which dissolved only TMAH 1% into example of comparison 1 ultrapure water, after processing a thermal oxidation film wafer by the same approach as an example 1, the oxide-film thickness of a thermal oxidation film wafer was measured. A result is shown in Table 1.

[0132]

[Table 1]

[0133] It turns out that the cleaning agent (example 1) of this invention hardly gives change to the oxide-film thickness of a thermal oxidation film wafer, i.e., do not have a bad influence on the insulator layer on the front face of a semi-conductor, so that clearly from Table 1. On the other hand, it turns out that the conventional cleaning agent (example 1 of a comparison) only containing the fourth class ammonium is dissolving or etching the oxide film remarkably.

[0134] 60 degrees C was immersed for 10 minutes into example 2 ultrapure water in the metal contamination wafer produced by the above-mentioned approach to the cleaning agent (pH7: neutral solution) which dissolved the diisobutyl dimethyl butynediol polyoxy-ethylene-glycol ether (it is hereafter written as a surface active agent 12.) whose number of average mols of an oxyethylene radical [p+p'] is 12 0.001% in the

above-mentioned general formula [6] which is a nonionic surface active agent. Then, the wafer was pulled up, and after carrying out a rinse for 10 minutes and carrying out spin desiccation with ultrapure water, in order to evaluate impurity (copper) removal capacity, the amount of copper atomic adsorption of a metal contamination wafer front face (residual copper concentration) was measured. A result is shown in Table 2.

[0135] Except having used the cleaning agent (pH7: neutral solution) which dissolved the dodecyl sulfonic acid sodium which be an anionic surface active agent 0.001% into example of comparison 2 ultrapure water, after processing a metal contamination wafer by the same approach as an example 2, in order to evaluate impurity (copper) removal capacity, the amount of copper atomic adsorption of a metal contamination wafer front face (residual copper concentration) be measured. A result is collectively shown in Table 2.

[0136] The diisobutyl dimethyl butynediol polyoxy-ethylene-glycol ether whose number of average mols of an oxyethylene radical [p+p'] is 6 in the above-mentioned general formula [6] which are 0.4% and a nonionic surface active agent about a choline in example 3 ultrapure water (with a surface active agent 6 hereafter) it outlines. Except having used the cleaning agent (12 or more pH) which dissolved 0.001%, after processing a metal contamination wafer by the same approach as an example 2, in order to evaluate impurity (copper) removal capacity, the amount of copper atomic adsorption of a metal contamination wafer front face (residual copper concentration) was measured. A result is collectively shown in Table 2.

[0137] Except having used the cleaning agent (12 or more pH) which dissolved dodecylbenzenesulfonic acid (LION make) which is 0.4% and an anionic surface active agent about a choline 0.001% into example of comparison 3 ultrapure water, after processing a metal contamination wafer by the same approach as an example 2, the amount of copper atomic adsorption of a metal contamination wafer front face (residual copper concentration) was measured. A result is collectively shown in Table 2.

[0138] The diisobutyl dimethyl butynediol polyoxy-ethylene-glycol ether whose number of average mols of an oxyethylene radical [p+p'] is 8 in the above-mentioned general formula [6] which are 0.03% and a nonionic surface active agent about TMAH in example 4 ultrapure water (with a surface active agent 8 hereafter) it outlines. Scrub washing was carried out with the brush made from polyvinyl alcohol of high-speed rotation for 1 minute, sprinkling the cleaning agent (pH10.5) which dissolved 0.001% over the metal contamination wafer produced by the above-mentioned approach in the shape of a shower. Then, after it carries out the rinse of the wafer for 10 minutes and it carries out spin desiccation with ultrapure water, in order to evaluate impurity (copper)

removal capacity, the amount of copper atomic adsorption of a metal contamination wafer front face (residual copper concentration) was measured. A result is shown in Table 2.

[0139] Except having used ultrapure water instead of example of comparison 4 cleaning agent, after processing a metal contamination wafer by the same approach as an example 4, the amount of copper atomic adsorption of a metal contamination wafer front face (residual copper concentration) was measured. A result is collectively shown in Table 2.

[0140]

[Table 2]

[0141] It turns out that the cleaning agent (example 2) of this invention containing a nonionic surfactant can control remarkably the residual copper concentration of a metal contamination wafer front face as compared with the cleaning agent (example 2 of a comparison) only containing an anionic surfactant, and residual copper concentration can be controlled even if compared with the fourth class ammonium and the cleaning agent (example 3 of a comparison) containing an anionic surfactant so that clearly from Table 2. Moreover, it turns out that the cleaning agent (example 3) of this invention containing a nonionic surfactant and the fourth class ammonium can control remarkably the residual copper concentration of a metal contamination wafer front face as compared with the cleaning agent (example 3 of a comparison) containing the cleaning agent (example 2 of a comparison) only containing an anionic surfactant, and the fourth class ammonium and an anionic surfactant. Furthermore, the case (example 3) where only chemical washing is performed shows that the direction at the time of using chemical

washing and physical washing together (example 4) can remove copper more effectively. [0142] The diisobutyl dimethyl butynediol polyoxy-ethylene-glycol ether whose number of average mols of an oxyethylene radical $[p+p']$ is 5 in the above-mentioned general formula [6] which are 3% and a nonionic surface active agent about TMAH in example 5 ultrapure water (with a surface active agent 5 hereafter) it outlines. Except having used the cleaning agent (12 or more pH) which dissolved 0.05%, after processing a copper deposition wafer by the same approach as an example 5, the copper film thickness of a copper deposition wafer was measured. A result is collectively shown in Table 3.

[0143] Except having used the cleaning agent (pH10) which dissolved diethanolamine 3% into example of comparison 5 ultrapure water, after processing a copper deposition wafer by the same approach as an example 5, the copper film thickness of a copper deposition wafer was measured. A result is collectively shown in Table 3.

[0144]

[Table 3]

[0145] Since the nonionic surfactant which is a cleaning agent of this invention, and the cleaning agent (example 5) containing the fourth class ammonium hardly affect the copper film thickness of a copper body product wafer front face, it turns out that neither the dissolution nor etching carries out copper, so that clearly from Table 3. On the other hand, it turns out that the cleaning agent (example 5 of a comparison) which does not contain a nonionic surface active agent although the second class amine is included is dissolving or etching copper remarkably.

[0146] TMAH is indicated to be 0003% in example 6 ultrapure water by the following general formula [7] which is a nonionic surfactant. Diisobutyl dimethyl butynediol polyoxypropylene-polyoxyethylene glycol ether whose number of average mols of an oxypropylene radical $[q+q']$ the number of average mols of an oxyethylene radical $[p+p']$ is 6, and is 2 [0147]

[Formula 50]

[0148] (It is hereafter written as a surfactant 6-2.) The particle contamination thermal oxidation film wafer and particle contamination copper deposition wafer which were produced by the above-mentioned approach were immersed in the cleaning agent (pH9) which dissolved 0.03% for 10 minutes at 60 degrees C, carrying out the seal of approval of the 1MHz RF. Then, the wafer was pulled up, and after carrying out a rinse for 10 minutes and carrying out spin desiccation with ultrapure water, in order to evaluate impurity (particle) removal capacity, the number of particle of a particle contamination thermal oxidation film wafer and a particle contamination copper deposition wafer was measured. A result is shown in Table 4.

[0149] Except having used the cleaning agent (pH9) which dissolved the stearyl chloride dimethylammonium which is 0.003% and a cationic surface active agent about TMAH 0.03% into example of comparison 6 ultrapure water, after processing a particle contamination thermal oxidation film wafer and a particle contamination copper deposition wafer by the same approach as an example 6, the number of particle of a particle contamination thermal oxidation film wafer and a particle contamination copper deposition wafer was measured. A result is collectively shown in Table 4.

[0150]

[Table 4]

[0151] The particle the number of particle which carries out adsorption survival on a thermal oxidation film wafer front face carries out [particle] adsorption survival on 30 and a copper deposition wafer front face is 5, and the nonionic surfactant which is a cleaning agent of this invention so that clearly from Table 4, and the cleaning agent (example 6) containing the fourth class ammonium are understood that the particle removal effectiveness is remarkably high also when it is any. On the other hand, the particle the number of particle which carries out adsorption survival on a thermal

oxidation film wafer front face carries out [particle] adsorption survival on 1200 and a copper deposition wafer front face is 202, and a cationic surfactant and the cleaning agent (example 6 of a comparison) containing the fourth class ammonium are understood that the particle removal effectiveness is low also when it is any.

[0152] The copper deposition wafer produced by the above-mentioned approach to the cleaning agent (pH11) which dissolved the diisobutyl dimethyl butynediol polyoxy-ethylene-glycol ether whose number of average mols of an oxyethylene radical [p+p'] is 4 0.05% in the above-mentioned general formula [6] which are 3% and a nonionic surface active agent about ammonia was immersed for 30 minutes at the room temperature (25 degrees C) into example 7 ultrapure water. Then, a wafer is pulled up, with ultrapure water, the rinse was carried out for 10 minutes and spin desiccation was carried out.

[0153] Diisobutyl dimethyl butynediol polyoxypropylene glycol ether whose number of average mols of an oxypropylene radical [q+q'] diethanolamine is indicated to be 3% in example 8 ultrapure water by the following general formula [8] which is a nonionic surfactant, and is 4 [0154]

[Formula 51]

[0155] The copper deposition wafer was processed by the same approach as an example 7 except having used the cleaning agent (pH10) which dissolved 0.05%.

[0156]

[Effect of the Invention] If the approach of washing a semi-conductor front face is offered and the penetrant remover of this invention is used, without this invention's being able to remove like the above the impurity which carries out adsorption survival on the semi-conductor front face on which copper wiring was given, and corroding and oxidizing copper wiring or starting a surface dry area, many problems at the time of semi-conductor manufacture are solvable.

TECHNICAL FIELD

[Field of the Invention] This invention relates to the cleaning agent and the washing approach on a semi-conductor front face and the front face of a semi-conductor where copper wiring was especially given to the front face.

PRIOR ART

[Description of the Prior Art] In recent years, detailed-ization is progressing with high integration and the structure of LSI is the multilayer structure which metal wiring etc. put on the semi-conductor front face in many steps. Moreover, modification in copper with more low electric resistance (Cu) from the aluminum of the former [wiring / which is used] is proposed.

[0003] The so-called chemical physical polish technique (Cu-CMP) which grinds and carries out flattening of the semi-conductor substrate physically is used for the process which manufactures the semi-conductor which has the multilayer structure by which copper wiring was continued and given to the multilayer on the front face, oxidizing Metal Cu.

[0004] On the other hand, the insulator layer (silicon oxide) which isolates Cu wiring and each Cu wiring is in the unreserved condition, and the wafer front face after a Cu-CMP process is polluted by a lot of impurity metals and particle by the semi-conductor front face after a Cu-CMP process. Cu impurity metal contamination is shaved [Cu] by CMP originates in adsorbing on an insulator layer and remaining as oxidization copper, and particle contamination originates in the slurry used at a CMP process for polish.

[0005] Thus, if copper oxide remains on an insulator layer, a copper element is spread in an insulator layer in heat treatment at a back process, the property of a device deteriorates because insulation falls, and a device will be destroyed in order for isolated wiring to raise connection, i.e., short-circuit, when contamination is remarkable. Therefore, before progressing to degree process, it is necessary to remove copper oxide. Moreover, in order for particle contamination to have a bad influence on degree process similarly, it is necessary to remove as much as possible.

[0006] In order to remove the above-mentioned **** impurity and particle by the above reason, the washing process after a Cu-CMP process is indispensable.

[0007] In the washing process after a Cu-CMP process, if the acid penetrant removers (a hydrochloric acid, fluoric acid, etc.) usually used as a penetrant remover for semi-conductors are used conventionally, in order to dissolve not only copper oxide but the metal copper of wiring which adhered on the insulator layer and to cause corrosion and an open circuit of wiring, use of the acid penetrant remover concerned is not desirable. Furthermore, when an acid solution is used, a semi-conductor front face and particle pay well electrostatic, and the problem of particle being not only unremovable, but causing reverse adsorption also has them. Moreover, although the alkaline penetrant

remover which a semi-conductor front face and particle **** for removal of particle mutually electrostatic is generally confirmed, when penetrant removers which contained the metal ion as a source of alkali, such as a sodium hydroxide and a potassium hydroxide, are used, these metals will stick to an insulator layer (silicon oxide) front face, and an insulating property will be degraded. Moreover, copper solvent power cannot use strongly the penetrant remover of the inorganic alkali (aqueous ammonia etc.) which does not contain a metal ion among alkaline penetrant removers.

[0008] On the other hand, although the penetrant remover containing the fourth class ammonium does not corrode copper wiring and has the advantage that the removal effectiveness of particle is also high, since the fourth class ammonium is strong-base nature, it has the fault of the etching force over an insulator layer being strong, and damaging the front face which carried out flattening at the CMP process. In order to cancel such a fault, by adding a hydrogen peroxide to the fourth class ammonium, it is known that it is possible to make an etch rate late. However, in this case, by the oxidizing power of a hydrogen peroxide, the front face of copper wiring oxidizes and the problem that conductivity will worsen arises.

[0009] Thus, the penetrant remover which can remove a surface impurity did not exist until now, without having not caused the corrosion or oxidation of copper wiring for the semi-conductor substrate which gave copper wiring, and starting a surface dry area.

EFFECT OF THE INVENTION

[Effect of the Invention] If the approach of washing a semi-conductor front face is offered and the penetrant remover of this invention is used, without this invention's being able to remove like the above the impurity which carries out adsorption survival on the semi-conductor front face on which copper wiring was given, and corroding and oxidizing copper wiring or starting a surface dry area, many problems at the time of semi-conductor manufacture are solvable.

TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] This invention offers the cleaning agent and the washing approach of removing the impurity of the front face concerned effectively, without not having been made in view of the above-mentioned **** situation, and not causing the corrosion or oxidation of copper wiring for a semi-conductor front face and the semi-conductor front face where copper wiring was especially given to the front face, and starting a surface dry area.

MEANS

[Means for Solving the Problem] This invention consists of the following configurations.

[0012] (1) The cleaning agent for semi-conductor front faces with which copper wiring was given to the front face which comes to contain a nonionic surfactant.

[0013] (2) The washing approach on the front face of a semi-conductor characterized by processing the semi-conductor front face where copper wiring was given to the front face with the cleaning agent which comes to contain a nonionic surfactant that copper wiring was given to the front face.

[0014] (3) The semi-conductor which was obtained by processing the semi-conductor front face where copper wiring was given to the front face with the cleaning agent which comes to contain a nonionic surfactant and with which copper wiring was given to the front face.

[0015] As a result of repeating research wholeheartedly that this invention person etc. should attain the above-mentioned purpose, by washing the semi-conductor front face where copper wiring was given using the cleaning agent containing a nonionic surfactant The oxidation copper which is adsorbing on an insulator layer or copper wiring, and an impurity like particle can be removed effectively, without being able to control the etch rate of an insulator layer, and not causing the corrosion or oxidation of copper wiring, and starting a surface dry area, Furthermore, such effectiveness is [0016] in the molecule as a nonionic surfactant.

[Formula 23]

[0017] When especially the thing that comes out and has the acetylenic group shown used the fourth class ammonium together in a desirable thing list also especially in such a surfactant and nitrogen-containing alkalinity compounds, such as ammonia, the first class, the third class amine, or the fourth class ammonium, based on a header and discovery of these single strings, it came to complete this invention for the effectiveness being promoted further.

[0018] Although each thing known conventionally is used as a nonionic surfactant in this invention, it is [0019] in the molecule.

[Formula 24]

[0020] What comes out and has the radical (acetylenic group) shown is desirable, and it is [0021] especially in a molecule.

[Formula 25]

[0022] What comes out and has the radical (acetylenic group) shown and a polyoxyalkylene group is desirable.

[0023] As the polyoxyalkylene group concerned, what is shown, for example by the following general formula [1] is mentioned.

[0024]

[Formula 26]

[0025] (X shows an alkylene group among a formula and y shows a positive integer) .

[0026] as the alkylene group shown by X in a general formula [1] — the low-grade alkylene group of the shape of a straight chain, the shape of branching, and the annular carbon numbers 1-6 — desirable — for example, a methylene group and ethylene, a propylene radical, a butylene radical, a methyl methylene group, ethyl ethylene, a methyl ethylene radical, a methyl propylene radical, an ethyl propylene radical, and a pentene radical — it passes, a xylene radical etc. is mentioned to a xylene radical a cyclo pentene radical, and cyclo, and ethylene or especially a propylene radical is desirable especially. Moreover, since a positive integer is shown, it is 1-8 preferably, foaming is usually suppressed also when the thing of 2-8 has low cellularity and y uses together with physical washing especially, 1-10, and, and it is hard to generate a trouble with a bubble, y is especially desirable. In addition, all of y oxy-alkylene groups may be the same, and they may consist of two sorts or more than it. In the oxy-alkylene group, shown by $-(X-O)-$ in a general formula [1], an oxyethylene radical, an oxypropylene radical, etc. are desirable, for example, and what consists only of an oxyethylene radical, for example, the thing which consists only of an oxypropylene radical, especially the thing that consists of combination of an oxyethylene radical and an oxypropylene radical are desirable as a polyoxyalkylene group shown by $-(X-O)_y-$. In addition, when it is what consists of combination of an oxyethylene radical and an oxypropylene radical, the oxyethylene radical of both ratio is usually 70% or more preferably 50% or more.

[0027] It is [0028] in the above-mentioned **** and a molecule.

[Formula 27]

[0029] As an example of a nonionic surfactant of coming out and having the radical shown and the polyoxyalkylene group shown by said general formula [1], what is shown, for example by the following general formula [2] is mentioned.

[0030]

[Formula 28]

[0031] X1 shows a low-grade alkylene group among [type, n shows a positive integer, R1 and R2 show independently a hydrogen atom, a hydroxyl group, an alkyl group, or a hydroxyalkyl radical, respectively, and R5 shows the radical shown by a hydrogen atom, the hydroxyl group, the alkyl group, the hydroxyalkyl radical, or the following general formula [3].

[0032]

[Formula 29]

[0033] (R3 and R4 show independently a hydrogen atom, a hydroxyl group, an alkyl group, or a hydroxyalkyl radical among a formula, respectively, X2 shows a low-grade alkylene group, and m shows a positive integer.)]

[0034] The low-grade alkylene group shown by X1 and X2 in the above-mentioned general formula [2] and [3] is the same as X in the **** general formula [1] mentioned above. Moreover, m and n are the same as y in the **** general formula [1] similarly mentioned above. In addition, when R5 in a general formula [2] is a general formula [3], it is 2-16 preferably, and since foaming is suppressed especially also when the thing of 4-16 has low cellularity and uses together with physical washing, 2-20, and, and it is hard to generate a trouble with a bubble, it is usually especially desirable [the sum total of m and n].

[0035] Also in the nonionic surface active agent shown by the above-mentioned **** general formula [2], that X1 and whose X2 are ethylene or/and a propylene radical is desirable. As these desirable things, what is shown, for example by the following general formula [2'] is mentioned.

[0036]

[Formula 30]

[0037] R1 and R2 are the same as the above among [type, r and s show 0 or a positive integer independently, respectively, and R5' shows the radical shown by a hydrogen atom, the hydroxyl group, the alkyl group, the hydroxyalkyl radical, or the following general formula [3'].

[0038]

[Formula 31]

[0039] (R3 and R4 are the same as the above among a formula, and r' and s' show 0 or a positive integer independently, respectively.) However, r, s, r', and s' remove the case of 0 to coincidence.]

[0040] Especially the thing whose radical shown by R5' in a general formula [2'] is a general formula [3'] especially, i.e., the thing shown by the following general formula [2''], is desirable.

[0041]

[Formula 32]

[0042] (a formula — inside — R — one — R — two — R — three — R — four — R — five — r — r — ' — s — and — s — ' — the above — being the same .)

[0043] In addition, it sets to the above-mentioned general formula [2'] and [2''], and is [0044].

[Formula 33]

[0045] The thing (the so-called block copolymer) and oxyethylene radical, and oxypropylene radical which consist of **, r blocks of an oxyethylene radical, and s

blocks of an oxypropylene radical join together in random order, and the former total means that (the so-called random copolymer) whose latter total is s pieces by r pieces. Moreover, the above-mentioned general formula [3'] and [0046] in [2"]
[Formula 34]

[0047] It is the same as that of **.

[0048] the nonionic surfactant concerning this invention — the very thing — it can prepare easily by the well-known approach. Namely, the glycol compound shown in U.S. Pat. No. 3291607 by the following general formula [2-1] according to the approach of a publication in order to, prepare the compound whose radical shown by R5 in a general formula [2] is a general formula [3] for example, and [0049]
[Formula 35]

[0050] (R1-R4 are the same as the above among a formula.) What is necessary is just to make the following general formula [2-2] or/and the alkylene oxide corresponding to [3-1] react.

[0051]

[Formula 36]

[0052] And [0053]

[Formula 37]

[0054] (X1, X2, n, and m are the same as the above among a formula.)

[0055] as the alkyl group shown by R1-R5, and R5' in the above-mentioned formula [2], [3], [2'], [3'], and [2"] — saturation — partial saturation — ***** — the shape of a straight chain, the shape of branching, and the annular carbon numbers 1-10 — desirable — 1-6 — it is 1-3 still more preferably. Specifically For example, a methyl group, an ethyl group, n-propyl group, n-butyl, n-pentyl radical, n-hexyl group, n-octyl radical, n-nonyl radical, Saturation straight chain alkyl groups, for example, iso-propyl groups,

such as n-deca nil radical, iso-butyl, sec-butyl, tert-butyl, an iso-pentyl radical, A sec-pentyl radical, a tert-pentyl radical, a neopentyl radical, an iso-hexyl group, Saturation branching alkyl groups, such as a sec-hexyl group and a tert-hexyl group, For example, annular alkyl groups, for example, a vinyl group, such as a cyclopentyl group and a cyclohexyl radical, Partial saturation branching alkyl groups, such as partial saturation straight chain alkyl groups, for example, an iso-propenyl radical, such as n-propenyl radical and n-butenyl group, an iso-butenyl group, a sec-butenyl group, and a tert-butenyl group, are mentioned. As a hydroxyalkyl radical, 1-3, the thing by which only the hydrogen atom of the end was more preferably permuted with the hydroxyl group are preferably mentioned 1 or more than it among the hydrogen atoms of the arbitration of these alkyl groups.

[0056] In addition, it is 1-16 preferably, and since cellularity is low, foaming is suppressed also when it uses together with physical washing, 1-20, and, and it is hard to generate a trouble with a bubble, especially the thing of 4-16 is usually especially desirable [the sum total of r, s, r' and s']. The thing whose s and s' is 0-2 independently, respectively and whose r and r' is 4-6 independently especially, respectively is more desirable.

[0057] As an example of a nonionic surface active agent of having an acetylenic group in a molecule, it is the diisobutyl dimethyl butynediol polyoxy-ethylene-glycol ether (1, 4-diisobutyl-1, 4-dimethylbut-2-yn diol polyoxyethylene glycol ether) in this invention shown, for example by the following general formula [6].

[0058]

[Formula 38]

[0059] the inside of [type, and the total (p+p') of p and p' — usually — 1-20 — desirable — 1-16 — it is 4-16 more preferably.] [0060] For example, the diisobutyl dimethyl butynediol polyoxyethylene / polyoxypropylene glycol ether shown by the following general formula [7] (1, 4-diisobutyl-1, 4-dimethylbut-2-yn diol polyoxyethylene-polyoxypropylene glycol ether)

[0061]

[Formula 39]

[0062] the inside of [type, and the total ($p+q+p'+q'$) of p , q , p' , and q' — usually — 1-20 — desirable — 1-16 — it is 4-16 more preferably.] [0063] For example, diisobutyl dimethyl butynediol polyoxypropylene glycol ether shown by the following general formula [8] (1, 4-diisobutyl-1, 4-dimethylbut-2-yn diol polyoxypropylene glycol ether)

[0064]

[Formula 40]

[0065] the inside of [type, and the total ($q+q'$) of q and q' — usually — 1-20 — desirable — 1-16 — it is 4-16 more preferably.] ** is mentioned.

[0066] The thing or commercial item prepared by the **** approach mentioned above, or any is sufficient as the nonionic surfactant used in this invention. The above-mentioned **** nonionic surfactant may be used independently, or two or more sorts, it may combine suitably and it may be used.

[0067] That the amount of the nonionic surface active agent used should just be more than critical micelle concentration, if thinner than it, the rate of etching will become quick and effectiveness will fade. Although there is no ***** generally as the concrete amount used since it changes with classes of surfactant, it is usually 1 ppm or more, and there is especially no upper limit, for example. However, when economical efficiency etc. is taken into consideration, 1-10000 ppm is desirable and is 10-1000 ppm more preferably.

[0068] As the ammonia in this invention, the first class, or the third class amine, what is shown, for example by the following general formula [4] is mentioned.

[0069]

[Formula 41]

[0070] (R11, R12, and R13 show independently a hydrogen atom, a low-grade alkyl group, or a hydroxy low-grade alkyl group among a formula, respectively.)

[0071] As a low-grade alkyl group shown by R11-R13 in a general formula [4] The thing of the shape of a straight chain, the shape of branching, and the annular carbon numbers 1-6 is mentioned. For example, specifically For example, a methyl group, an ethyl group, n-propyl group, an iso-propyl group, n-butyl, iso-butyl, sec-butyl, tert-butyl, n-pentyl radical, an iso-pentyl radical, a sec-pentyl radical, a tert-pentyl radical, a neopentyl radical, n-hexyl group, an iso-hexyl group, a sec-hexyl group, a tert-hexyl group, a cyclopentyl group, a cyclohexyl radical, etc. are mentioned. As a hydroxy low-grade alkyl group shown by R11-R13 in a general formula [4] That by which the hydrogen atom of the end was preferably permuted with the hydroxyl group is mentioned 1 or more than it among the hydrogen atoms of the arbitration of the above-mentioned **** low-grade alkyl group. Specifically For example, a hydroxymethyl group, hydroxyethyl radical, 3-hydroxy-n-propyl group, 4-hydroxy-n-butyl, 1-methyl-2-hydroxyethyl radical, 2-methyl-3-hydroxypropyl radical, 1, and 1-dimethyl-2-hydroxyethyl radical etc. is mentioned.

[0072] As an example of the compound shown by the general formula [4], for example, ammonia, For example, primary amine, such as monomethylamine, ethylamine, n propylamine, and n butylamine, For example, dimethylamine, diethylamine, a methylethyl amine, G n propylamine, The second class amines, for example, a trimethylamine, such as G n butylamine, triethylamine, The third class amines, such as methyl diethylamine, tree n propylamine, and tree n butylamine, For example, third class hydroxy amines, such as second class hydroxy amines, for example, triethanolamine etc., such as first-class hydroxy amines, for example, diethanolamine etc., such as monoethanolamine, etc. are mentioned.

[0073] As the fourth class ammonium in this invention, what is shown, for example by the following general formula [5] is mentioned.

[0074]

[Formula 42]

[0075] (R6-R9 show among a formula the hydrocarbon residue which may have the hydroxyl group independently, respectively, and M- shows an anion.)

[0076] As hydrocarbon residue of the hydrocarbon residue which may have the

hydroxyl group shown by R6-R9 in a general formula [5], any of aliphatic series, aromatic series, aroma aliphatic series, or an alicycle group are sufficient, and as aliphatic series in aliphatic series and aroma aliphatic series, it may be [being saturation] unsaturated, or the shape of the shape of a straight chain and branching has. As a typical thing of these, the alkyl group of the shape of a straight chain, the shape of branching, annular saturation, or partial saturation, an aralkyl radical, an aryl group, etc. are mentioned, for example. As an alkyl group, the low-grade alkyl group of 1-6, especially the low-grade alkyl group of carbon numbers 1-4 usually have a desirable carbon number. Specifically For example, a methyl group, an ethyl group, n-propyl group, an iso-propyl group, n-butyl, iso-butyl, sec-butyl, tert-butyl, n-pentyl radical, an iso-pentyl radical, a sec-pentyl radical, a tert-pentyl radical, A neopentyl radical, n-hexyl group, an iso-hexyl group, a sec-hexyl group, A tert-hexyl group, a cyclopentyl group, a cyclohexyl radical, a vinyl group, n-propenyl radical, an iso-propenyl radical, n-butenyl group, an iso-butenyl group, a sec-butenyl group, a tert-butenyl group, etc. are mentioned. As an aralkyl radical, the thing of carbon numbers 7-12 is usually mentioned, and, specifically, benzyl, a phenethyl radical, a phenylpropyl radical, phenyl butyl, a phenyl hexyl group, a methylbenzyl radical, a methyl phenethyl radical, ethyl benzyl, etc. are mentioned. As an aryl group, the thing of carbon numbers 6-14 is usually mentioned, a phenyl group, o-tolyl group, m-tolyl group, p-tolyl group, 2, 3-xylyl group, 2, 4-xylyl group, 2, 5-xylyl group, 2, 6-xylyl group, 3, 5-xylyl group, a naphthyl group, an anthryl radical, etc. specifically mention, and it is ****. In addition, in the ring of the above-mentioned **** aryl group or an aralkyl radical, you may have low-grade alkyl groups, such as a methyl group and an ethyl group, a halogen atom, a nitro group, the amino group, etc. as a substituent. That by which the above-mentioned hydrogen atom of hydrocarbon residue was permuted with the hydroxyl group as hydrocarbon residue which has a hydroxyl group is mentioned. As an anion shown by M- in a general formula [5], OH- etc. is mentioned, for example.

[0077] As an example of the above-mentioned fourth class ammonium of ****, the following are mentioned, for example. Tetramethylammonium hydroxide (TMAH), hydroxylation trimethyl-2-hydroxyethyl ammonium (choline), Hydroxylation tetraethylammonium, hydroxylation tetrapropylammonium, Hydroxylation tetrabutylammonium, hydroxylation monomethyl triethyl ammonium, Hydroxylation dimethyl diethyl ammonium, hydroxylation trimethyl monoethyl ammonium, Hydroxylation monomethyl TORIPURO pill ammonium, hydroxylation dimethyl dipropyl ammonium, Hydroxylation trimethyl monopropyl ammonium, hydroxylation monomethyl tributyl ammonium, Hydroxylation dimethyl dibutyl ammonium,

hydroxylation trimethyl monobutyl ammonium, Hydroxylation monoethyl TORIPURO pill ammonium, hydroxylation diethyl dipropyl ammonium, Hydroxylation triethyl monopropyl ammonium, hydroxylation monoethyl tributyl ammonium, Hydroxylation diethyl dibutyl ammonium, hydroxylation triethyl monobutyl ammonium, Hydroxylation monopropyl tributyl ammonium, hydroxylation dipropyl dibutyl ammonium, Hydroxylation TORIPURO pill monobutyl ammonium, hydroxylation triethyl-2-hydroxyethyl ammonium, Hydroxylation TORIPUROPIRU-2-hydroxyethyl ammonium, hydroxylation tributyl-2-hydroxyethyl ammonium, Hydroxylation trimethyl-3-hydroxypropyl ammonium, hydroxylation triethyl-3-hydroxypropyl ammonium, Hydroxylation TORIPUROPIRU-3-hydroxypropyl ammonium, hydroxylation tributyl-3-hydroxypropyl ammonium, Hydroxylation trimethyl-4-hydroxy butyl ammonium, hydroxylation triethyl-4-hydroxy butyl ammonium, Hydroxylation TORIPUROPIRU-4-hydroxy butyl ammonium, hydroxylation tributyl-4-hydroxy butyl ammonium, Hydroxylation trimethyl-3-hydroxy butyl ammonium, hydroxylation triethyl-3-hydroxy butyl ammonium, Hydroxylation TORIPUROPIRU-3-hydroxy butyl ammonium, hydroxylation tributyl-3-hydroxy butyl ammonium, Hydroxylation dimethyl ethyl-2-hydroxyethyl ammonium, hydroxylation methyl diethyl-2-hydroxyethyl ammonium, Hydroxylation dimethyl ethyl-3-hydroxypropyl ammonium, hydroxylation methyl diethyl-3-hydroxypropyl ammonium, Hydroxylation dimethyl ethyl-4-hydroxy butyl ammonium, hydroxylation methyl diethyl-4-hydroxy butyl ammonium, Hydroxylation dimethyl ethyl-3-hydroxy butyl ammonium, hydroxylation methyl diethyl-3-hydroxy butyl ammonium, Hydroxylation JIMECHIRUJI (2-hydroxyethyl) ammonium, hydroxylation JIMECHIRUJI (3-hydroxypropyl) ammonium, Hydroxylation JIMECHIRUJI (3-hydroxy butyl) ammonium, hydroxylation JIMECHIRUJI (4-hydroxy butyl) ammonium, Hydroxylation JIECHIRUJI (2-hydroxyethyl) ammonium, hydroxylation JIECHIRUJI (3-hydroxypropyl) ammonium, Hydroxylation JIECHIRUJI (3-hydroxy butyl) ammonium, hydroxylation JIECHIRUJI (4-hydroxy butyl) ammonium, Hydroxylation methyl ECHIRUJI (2-hydroxyethyl) ammonium, hydroxylation methyl ECHIRUJI (3-hydroxypropyl) ammonium, Hydroxylation JIECHIRUJI (3-hydroxy butyl) ammonium, hydroxylation methyl ECHIRUJI (4-hydroxy butyl) ammonium, Hydroxylation MECHIRUTORI (2-hydroxyethyl) ammonium, hydroxylation ECHIRUTORI (2-hydroxyethyl) ammonium, Hydroxylation pro PIRUTORI (2-hydroxyethyl) ammonium, hydroxylation BUCHIRUTORI (2-hydroxyethyl) ammonium, Hydroxylation MECHIRUTORI (3-hydroxypropyl) ammonium, hydroxylation ECHIRUTORI (3-hydroxy butyl) ammonium, Hydroxylation

MECHIRUTORI (4-hydroxy butyl) ammonium, hydroxylation ECHIRUTORI (4-hydroxy butyl) ammonium, hydroxylation MECHIRUTORI (3-hydroxy butyl) ammonium, hydroxylation ECHIRUTORI (3-hydroxy butyl) ammonium. Also in these, tetramethylammonium hydroxide (TMAH), especially hydroxylation trimethyl-2-hydroxyethyl ammonium (choline), etc. are desirable.

[0078] The fourth class ammonium shown by the compound shown by the above-mentioned general formula [4] or the general formula [5] may be used independently, or two or more sorts, it may combine suitably and it may be used.

[0079] Since the amount of the fourth class ammonium used shown by the compound shown by the general formula [4] used in this invention or the general formula [5] changes with classes, it does not generally have *****, but since the rate of etching becomes slow by low concentration not much and effectiveness fades, it is usually more than 0.003% (w/v), for example. Moreover, although there is especially no upper limit, when economical efficiency etc. is taken into consideration, 0.003 - 10% (w/v) is desirable, and is 0.05 - 1% (w/v) still more preferably 0.01 to 6% (w/v) more preferably.

[0080] (1) As a desirable mode of the cleaning agent of this invention, the following are mentioned, for example.

(a) The fourth class ammonium shown as a nitrogen-containing alkalinity compound by the ammonia shown by the general formula [4], the first class, the third class amine, or the general formula [5], and [0081]

[Formula 43]

[0082] (— R6, R7, R8, R9, R11, R12, R13, and M— are the same as the above among a formula. D) — the nonionic surfactant shown by the (b) general formula [2] — 0083]

[Formula 44]

[0084] (— R1, R2, R5, X1, and n are the same as the above among a formula.) — cleaning agent for semi-conductors which becomes as a major component.

[0085] (2) as the more desirable mode of the cleaning agent of this invention — a less or equal — like — come out.

(a') The fourth class ammonium shown by the general formula [5], and [0086]
[Formula 45]

[0087] (— R6, R7, R8, R9, and M— are the same as the above among a formula. D) — the nonionic surfactant shown by the general formula (b') [2'] — 0088]
[Formula 46]

[0089] (— R1, R2, R5', and r and s are the same as the above among a formula.) — cleaning agent for semi-conductors which becomes as a major component.

[0090] (3) as the still more desirable mode of the cleaning agent of this invention — a less or equal — like — come out.

(a'') The fourth class ammonium shown by the general formula [5'], and [0091]
[Formula 47]

[0092] (— R6, R7, R8, and R9 are the same as the above among a formula. D) — the nonionic surfactant shown by the general formula (b'') [2''] — 0093]
[Formula 48]

[0094] (— a formula — inside — R — one — R — two — R — three — R — four — r — s — r — ' — and — s — ' — the above — being the same .) — cleaning agent for semi-conductors which becomes as a major component.

[0095] In addition, in the above-mentioned mode, especially the case where a methyl group, and R2 and R4 are [R1 and R3 in a general formula [2'']] isobutyl radicals, and all of R6-R9 in a general formula [5'] are methyl groups, or three are a methyl group among those, and the one remaining is 2-hydroxyethyl radical is desirable.

[0096] Although the cleaning agent of this invention can be used also as cleaning agents, such as not only a semi-conductor but a printed circuit board, and a LCD substrate, especially the above-mentioned **** mode is useful to washing on the front face of a semi-conductor where copper wiring was given to the front face.

[0097] The cleaning agent of this invention is usually in the condition of a water solution, and is prepared by making water carry out the addition dissolution of the above-mentioned **** nonionic surfactant or a nonionic surfactant, and the nitrogen-containing alkalinity compound.

[0098] Thus, as for the prepared cleaning agent of this invention, it is desirable to perform filtration processing etc. before use. Moreover, although the water used here should just be refined by distillation, ion exchange treatment, etc., its so-called ultrapure water used in this field is more desirable.

[0099] the cleaning agent of this invention — alkalinity — desirable — usually — nine or more pH — desirable — pH 9-12 — it is pH 9.5-10.5 more preferably. Since a possibility of etching SiO₂ which is an interlayer insulation film decreases more and electric repulsion with a semi-conductor front face and particle becomes large further by considering as such pH range, particle and the cleaning effect of CuO improve.

[0100] In order to consider as the **** pH range which described the cleaning agent of this invention above, as long as it requires, carboxylic acids, such as pH regulator usually used in this field, for example, a citric acid, oxalic acid, a phthalic acid, and a tartaric acid, these derivatives or these salts, a phosphoric acid, a phosphoric-acid derivative, or a salt may be used.

[0101] Moreover, the cleaning agent of this invention has especially the desirable thing that has buffer capacity in above-mentioned **** pH within the limits. independent in what has buffer capacity by **** pH within the limits which itself described above among the above-mentioned **** pH modifiers, in order to give buffer capacity to the cleaning agent of this invention — or, even if it combines two or more sorts Or although you may use combining pH regulators other than this and it does not have buffer capacity in itself The thing which can give buffer capacity to the cleaning agent of this invention, or the thing which can give buffer capacity to the cleaning agent of this invention by using it combining a nitrogen-containing alkalinity compound may be used by using two or more sorts, combining. In addition, especially when only the above-mentioned **** nitrogen-containing alkalinity compound can give buffer capacity to the cleaning agent of this invention, it cannot be overemphasized that it is not necessary to use pH regulator.

[0102] Since it changes as amount of these pH regulator used with classes of pH

regulator to be used, there is no ***** generally, but when the cleaning agent of this invention is made to add, it is 0.0001 - 10% (w/v) usually [of the cleaning agent whole quantity] 0.001 - 1% (w/v) preferably that what is necessary is just the amount which becomes **** pH within the limits which the cleaning agent concerned described above. [0103] Moreover, in the cleaning agent of this invention, the chelating agent which does not have the capacity to dissolve copper wiring may be added. By adding such a chelating agent, the copper oxide distributed in liquid can be solubilized, and re-adsorption can be suppressed, and Fe, aluminum, etc. which are the impurity of the slurry origin at a CMP process can also be removed from a front face. as the chelating agent which does not have the capacity to dissolve such copper wiring — ethylenediaminetetraacetic acid (EDTA), trans-1, and 2-diamino cyclohexane - N, N, N', and N' — phosphonic acid, such as carboxylic acids (methylene phosphonic acid) (EDTPO), for example, ethylenediamine tetrakis etc., such as -4 acetic acid (CyDTA) and nitrilotriacetic acid (NTA), is mentioned. Since it changes as amount of these chelating agents used with classes of chelating agent to be used, there is no ***** generally, but when the cleaning agent of this invention is made to add, it is 0.0001 - 1% (w/v) usually [of the cleaning agent whole quantity] 0.001 - 0.1% (w/v) preferably that what is necessary is just the amount which can do so the **** effectiveness which the cleaning agent concerned described above.

[0104] furthermore, the purpose which suppresses separation with the above-mentioned **** nonionic surfactant and the above-mentioned nitrogen-containing alkalinity compound in the cleaning agent of this invention — small quantity — for example, 0.1 - 1% (w/v) of organic solvent may usually be added preferably 0.01 to 5% (w/v). As an organic solvent, a methanol, ethanol, isopropyl alcohol, an acetone, etc. are mentioned, for example.

[0105] Into the cleaning agent of this invention, the reagents usually used in this field in addition to the above-mentioned **** nonionic surfactant, a nitrogen-containing alkalinity compound, pH regulator, a chelating agent, and an organic solvent can be used. Such reagents protect Cu of wiring, and are used in order to prevent the corrosion of Cu. For example, reducing agents, such as a hydrazine or its derivative, an ascorbic acid, formic acid, and formalin, For example, metallic corrosion inhibitors, such as benzotriazol or its derivative, and thiourea etc., Improve the wettability of a cleaning agent to a semi-conductor front face, and are used in order to raise a cleaning effect. They are surface active agents other than a nonionic surface active agent (for example, amphoteric surface active agents, such as cation system surface active agents, such as anion system surface active agents, such as dodecylbenzenesulfonic acid, and alkyl

trimethylammonium, and carboxy betaine etc.) etc.

[0106] What is necessary is just to use these reagents by the density range usually used in this field. For example, the amount of the reducing agent used is usually 0.05 - 1 % of the weight preferably 0.01 to 5% of the weight that what is necessary is just the amount which can prevent oxidation of Metal Cu. Moreover, it is 0.05 - 1 % of the weight preferably, and the amount of surfactants used other than a nonionic surfactant is [that what is necessary is just the amount which the amount of the metallic corrosion inhibitor used forms Metal Cu and weak coupling, and can control the solvent power of the cleaning agent to Cu] usually 0.001 - 0.1 % of the weight preferably 0.0001 to 1% of the weight 0.01 to 5% of the weight that what is necessary is just the amount in which the surface tension of a cleaning agent may be reduced.

[0107] What is necessary is just to process the washing approach of this invention with the cleaning agent of **** this invention which described above the semi-conductor front face where Cu wiring was given to the front face.

[0108] the very thing usually performed in this field as an approach of processing the semi-conductor front face where Cu wiring was given to the front face with the cleaning agent of this invention — specifically, approaches, such as DIP processing only immersed into a cleaning agent in a semi-conductor and sheet processing which sprinkles a cleaning agent over a semi-conductor in the shape of a shower, are mentioned that what is necessary is just the approach of washing a well-known semi-conductor front face.

[0109] Furthermore, in this invention, CuO can be more effectively removed by using physical washing together at the time of washing. Giving the semi-conductor front face where Cu wiring was given to the front face to a physical washing process under existence of the cleaning agent of this invention as the concrete approach of concomitant use etc. is mentioned.

[0110] In the above-mentioned approach, the approach of giving to a physical washing process as a condition in which the cleaning agent of this invention was made to specifically exist by the above-mentioned **** DIP processing, sheet processing, etc. as an approach in which the cleaning agent of this invention is made to exist etc. is mentioned. Moreover, brush scrub washing which washes a semi-conductor front face, for example, using the brush made from polyvinyl alcohol of high-speed rotation etc. as physical washing (process), megasonic washing using a RF, etc. are mentioned.

[0111] As more concrete technique in the case of using physical washing together For example, the method of performing physical washing, after considering as the condition of having taken out the semi-conductor out of the penetrant remover concerned after

being immersed into the cleaning agent of this invention, and having made the cleaning agent concerned existing in a semi-conductor front face, How to perform physical washing while the semi-conductor had been made immersed into the cleaning agent of this invention, The method of performing physical washing etc. is mentioned sprinkling the cleaning agent of this invention over the method of performing physical washing, or a semi-conductor front face, after considering as the condition of having sprinkled the cleaning agent of this invention over the semi-conductor front face, and having made the cleaning agent concerned existing in a semi-conductor front face.

[0112] When the cleaning agent of this invention containing a nonionic surfactant is used, the effectiveness of allowing neither the particle of the slurry origin which protects copper wiring and floats in a penetrant remover, nor the slag of an insulator layer etched slightly to come near is done so. When the cleaning agent of this invention which contains the fourth class ammonium and a nonionic surfactant especially is used, etching of the insulator layer by the fourth class ammonium can be reduced, the advantage of the fourth class ammonium with the high effectiveness of removing particle can be employed efficiently, without corroding copper wiring, therefore etching of an insulator layer is suppressed to the minimum, and a surface dry area is not started. And re-adsorption of the copper oxide which exfoliated is also prevented effectively.

[0113] Moreover, in ionic surfactants, such as cationicity, anionic, or both sexes, it may combine with a semi-conductor front face electrically, and washing may be barred, or the surface charge of the particle of the slurry origin which originally considers electric repulsion as a semi-conductor front face with alkalinity may be changed, and re-adsorption of particle may be caused.

[0114] As mentioned above, a nonionic surface active agent, especially the nonionic surface active agent which has an acetylenic group in a molecule, With this, furthermore, by for example, nitrogen-containing alkalinity compounds, such as ammonia, the first class, the third class amine, or the fourth class ammonium, and the penetrant remover which contains both of the fourth class ammonium even especially in inside Without not causing the corrosion or oxidation of copper wiring and starting a surface dry area, if the semi-conductor front face which gave copper wiring is washed, the impurity which is sticking to a front face can be removed and the effectiveness that surface cleanliness can be improved is especially done so notably.

[0115] As described above, although the cleaning agent of this invention is very useful to washing on the front face of a semi-conductor where copper wiring was given to the front face, its wiring of those other than copper, such as for example, not only a thing but aluminum wiring with which copper wiring was given, and a tungsten plug, is

usable also in washing on the front face of a semi-conductor given to the front face. Furthermore, the cleaning agent of this invention is applicable not only to a semi-conductor front face but washing of front faces, such as a printed circuit board and a LCD substrate, again.

[0116] Although an example and the example of a comparison are given to below, this invention is not limited at all by these.

[0117] In addition, the nonionic surfactant used in the example below is compoundable with the reaction of the glycol compound and alkylene oxide which correspond to U.S. Pat. No. 3291607 according to the approach of a publication.

[0118] Moreover, the thermal oxidation film wafer and metal contamination wafer which were used in this example and the example of a comparison, A copper deposition wafer, a particle contamination thermal oxidation film wafer, and a particle contamination copper deposition wafer use what was prepared by the following approaches, respectively. Moreover, the amount of adsorption (residual copper concentration) and the number of particle of a copper atom which are carrying out adsorption survival were measured by the following approaches, respectively on the thickness of the oxide film of a thermal oxidation film wafer, the thickness of the copper of a copper deposition wafer front face, and a metal contamination wafer front face.

[0119] [Thermal oxidation film wafer] After processing the 4 inch silicon wafer in the fluoric acid water solution 1% and removing the surface natural oxidation film, it heat-treated at 800 degrees C, and the thing in which the thermal oxidation film (silicon oxide, insulator layer) was formed on the wafer front face was used as the thermal oxidation film wafer. In addition, the thickness of the oxide film of the thermal oxidation film wafer concerned checked that it was 500A by the approach shown below.

[0120] [Metal contamination wafer] After having been immersed in the nitric-acid water solution which added the copper ion for 1 minute so that a thermal oxidation film wafer might be set to 1 ppm, and carrying out style backwashing by water during 10 minutes with ultrapure water, what carried out spin desiccation was used as the metal contamination wafer. In addition, to the metal contamination wafer concerned, it checked that the copper atom was carrying out 3×10^{14} atom / cm² adsorption survival by the approach shown below.

[0121] [Copper deposition wafer] The thing which made metal copper deposit on a thermal oxidation film wafer front face by the sputtering method was used as the copper deposition wafer. In addition, the thickness of the copper of the copper deposition wafer front face concerned checked that it was 1000A by the approach shown below.

[0122] [A particle contamination thermal oxidation film wafer and particle

contamination copper deposition wafer] After being immersed in the alumina slurry water solution for 1 minute 3% with a mean particle diameter of 0.2 micrometers, respectively and carrying out style backwashing by water during 10 minutes of a thermal oxidation film wafer or the copper deposition wafer with ultrapure water, what carried out spin desiccation was used as the particle contamination thermal oxidation film wafer or the particle contamination copper deposition wafer, respectively. in addition, the approach shown below — the particle contamination thermal oxidation film wafer concerned — particle — about 850 pieces / 4 inch wafer, and a particle contamination copper deposition wafer — particle — about 90 pieces / 4 inch wafer — it checked each carrying out adsorption survival.

[0123] [Thickness measurement method of an oxide film] It measured by the thickness gage (ellipsometer).

[0124] [Copper thickness measurement method] The wafer was divided into one half, the cross section was observed with the electron microscope, and copper thickness was measured.

[0125] The [amount (residual copper concentration) measuring method of copper atomic adsorption] On the wafer front face, after carrying out dissolution recovery of the copper which carried out adsorption survival in a fluoric acid-nitric-acid water solution, the copper concentration in this recovery liquid was measured with the atomic absorption method (graphite furnace atomic-absorption-analysis equipment). Based on the obtained measured value, the amount of adsorption (residual copper concentration) of a copper atom was calculated.

[0126] The [number measuring method of particle] The particle which is carrying out adsorption survival was measured with surface dust-particle-inspection equipment (particle counter) on the wafer front face.

[0127] In addition, in this example and the example of a comparison, all especially of % which expresses concentration as long as there is no notice, and ppm and ppb show a weight ratio. Moreover, all the water to be used was ultrapure water, and it was used after checking that copper was 0.01 or less ppb.

EXAMPLE

[Example] The diisobutyl dimethyl butynediol polyoxy-ethylene-glycol ether whose number of average mols of an oxyethylene radical [p+p'] tetramethylammonium hydroxide (TMAH) is indicated to be 1% in example 1 ultrapure water by the following general formula [6] which is a nonionic surface active agent, and is 10 [0129]

[Formula 49]

[0130] (— it is hereafter written as a surfactant 10.) — 60 degrees C was immersed in the cleaning agent (12 or more pH) which dissolved 0.03% for 10 minutes in the thermal oxidation film wafer produced by the above-mentioned approach. Then, the wafer was pulled up, and after carrying out a rinse for 10 minutes and carrying out spin desiccation with ultrapure water, in order to check the existence of the corrosion of an oxide film, the oxide-film thickness of a thermal oxidation film wafer was measured. A result is collectively shown in Table 1.

[0131] Except having used the cleaning agent (12 or more pH) which dissolved only TMAH 1% into example of comparison 1 ultrapure water, after processing a thermal oxidation film wafer by the same approach as an example 1, the oxide-film thickness of a thermal oxidation film wafer was measured. A result is shown in Table 1.

[0132]

[Table 1]

[0133] It turns out that the cleaning agent (example 1) of this invention hardly gives change to the oxide-film thickness of a thermal oxidation film wafer, i.e., do not have a bad influence on the insulator layer on the front face of a semi-conductor, so that clearly from Table 1. On the other hand, it turns out that the conventional cleaning agent (example 1 of a comparison) only containing the fourth class ammonium is dissolving or etching the oxide film remarkably.

[0134] 60 degrees C was immersed for 10 minutes into example 2 ultrapure water in the metal contamination wafer produced by the above-mentioned approach to the cleaning agent (pH7: neutral solution) which dissolved the diisobutyl dimethyl butynediol polyoxy-ethylene-glycol ether (it is hereafter written as a surface active agent 12.) whose number of average mols of an oxyethylene radical [p+p'] is 12 0.001% in the

above-mentioned general formula [6] which is a nonionic surface active agent. Then, the wafer was pulled up, and after carrying out a rinse for 10 minutes and carrying out spin desiccation with ultrapure water, in order to evaluate impurity (copper) removal capacity, the amount of copper atomic adsorption of a metal contamination wafer front face (residual copper concentration) was measured. A result is shown in Table 2.

[0135] Except having used the cleaning agent (pH7: neutral solution) which dissolved the dodecyl sulfonic acid sodium which be an anionic surface active agent 0.001% into example of comparison 2 ultrapure water, after processing a metal contamination wafer by the same approach as an example 2, in order to evaluate impurity (copper) removal capacity, the amount of copper atomic adsorption of a metal contamination wafer front face (residual copper concentration) be measured. A result is collectively shown in Table 2.

[0136] The diisobutyl dimethyl butynediol polyoxy-ethylene-glycol ether whose number of average mols of an oxyethylene radical $[p+p']$ is 6 in the above-mentioned general formula [6] which are 0.4% and a nonionic surface active agent about a choline in example 3 ultrapure water (with a surface active agent 6 hereafter) it outlines. Except having used the cleaning agent (12 or more pH) which dissolved 0.001%, after processing a metal contamination wafer by the same approach as an example 2, in order to evaluate impurity (copper) removal capacity, the amount of copper atomic adsorption of a metal contamination wafer front face (residual copper concentration) was measured. A result is collectively shown in Table 2.

[0137] Except having used the cleaning agent (12 or more pH) which dissolved dodecylbenzenesulfonic acid (LION make) which is 0.4% and an anionic surface active agent about a choline 0.001% into example of comparison 3 ultrapure water, after processing a metal contamination wafer by the same approach as an example 2, the amount of copper atomic adsorption of a metal contamination wafer front face (residual copper concentration) was measured. A result is collectively shown in Table 2.

[0138] The diisobutyl dimethyl butynediol polyoxy-ethylene-glycol ether whose number of average mols of an oxyethylene radical $[p+p']$ is 8 in the above-mentioned general formula [6] which are 0.03% and a nonionic surface active agent about TMAH in example 4 ultrapure water (with a surface active agent 8 hereafter) it outlines. Scrub washing was carried out with the brush made from polyvinyl alcohol of high-speed rotation for 1 minute, sprinkling the cleaning agent (pH10.5) which dissolved 0.001% over the metal contamination wafer produced by the above-mentioned approach in the shape of a shower. Then, after it carries out the rinse of the wafer for 10 minutes and it carries out spin desiccation with ultrapure water, in order to evaluate impurity (copper)

removal capacity, the amount of copper atomic adsorption of a metal contamination wafer front face (residual copper concentration) was measured. A result is shown in Table 2.

[0139] Except having used ultrapure water instead of example of comparison 4 cleaning agent, after processing a metal contamination wafer by the same approach as an example 4, the amount of copper atomic adsorption of a metal contamination wafer front face (residual copper concentration) was measured. A result is collectively shown in Table 2.

[0140]

[Table 2]

[0141] It turns out that the cleaning agent (example 2) of this invention containing a nonionic surfactant can control remarkably the residual copper concentration of a metal contamination wafer front face as compared with the cleaning agent (example 2 of a comparison) only containing an anionic surfactant, and residual copper concentration can be controlled even if compared with the fourth class ammonium and the cleaning agent (example 3 of a comparison) containing an anionic surfactant so that clearly from Table 2. Moreover, it turns out that the cleaning agent (example 3) of this invention containing a nonionic surfactant and the fourth class ammonium can control remarkably the residual copper concentration of a metal contamination wafer front face as compared with the cleaning agent (example 3 of a comparison) containing the cleaning agent (example 2 of a comparison) only containing an anionic surfactant, and the fourth class ammonium and an anionic surfactant. Furthermore, the case (example 3) where only chemical washing is performed shows that the direction at the time of using chemical

washing and physical washing together (example 4) can remove copper more effectively. [0142] The diisobutyl dimethyl butynediol polyoxy-ethylene-glycol ether whose number of average mols of an oxyethylene radical $[p+p']$ is 5 in the above-mentioned general formula [6] which are 3% and a nonionic surface active agent about TMAH in example 5 ultrapure water (with a surface active agent 5 hereafter) it outlines. Except having used the cleaning agent (12 or more pH) which dissolved 0.05%, after processing a copper deposition wafer by the same approach as an example 5, the copper film thickness of a copper deposition wafer was measured. A result is collectively shown in Table 3.

[0143] Except having used the cleaning agent (pH10) which dissolved diethanolamine 3% into example of comparison 5 ultrapure water, after processing a copper deposition wafer by the same approach as an example 5, the copper film thickness of a copper deposition wafer was measured. A result is collectively shown in Table 3.

[0144]

[Table 3]

[0145] Since the nonionic surfactant which is a cleaning agent of this invention, and the cleaning agent (example 5) containing the fourth class ammonium hardly affect the copper film thickness of a copper body product wafer front face, it turns out that neither the dissolution nor etching carries out copper, so that clearly from Table 3. On the other hand, it turns out that the cleaning agent (example 5 of a comparison) which does not contain a nonionic surface active agent although the second class amine is included is dissolving or etching copper remarkably.

[0146] TMAH is indicated to be 0003% in example 6 ultrapure water by the following general formula [7] which is a nonionic surfactant. Diisobutyl dimethyl butynediol polyoxypropylene-polyoxyethylene glycol ether whose number of average mols of an oxypropylene radical $[q+q']$ the number of average mols of an oxyethylene radical $[p+p']$ is 6, and is 2 [0147]

[Formula 50]

[0148] (It is hereafter written as a surfactant 6-2.) The particle contamination thermal oxidation film wafer and particle contamination copper deposition wafer which were produced by the above-mentioned approach were immersed in the cleaning agent (pH9) which dissolved 0.03% for 10 minutes at 60 degrees C, carrying out the seal of approval of the 1MHz RF. Then, the wafer was pulled up, and after carrying out a rinse for 10 minutes and carrying out spin desiccation with ultrapure water, in order to evaluate impurity (particle) removal capacity, the number of particle of a particle contamination thermal oxidation film wafer and a particle contamination copper deposition wafer was measured. A result is shown in Table 4.

[0149] Except having used the cleaning agent (pH9) which dissolved the stearyl chloride dimethylannmonium which is 0.003% and a cationic surface active agent about TMAH 0.03% into example of comparison 6 ultrapure water, after processing a particle contamination thermal oxidation film wafer and a particle contamination copper deposition wafer by the same approach as an example 6, the number of particle of a particle contamination thermal oxidation film wafer and a particle contamination copper deposition wafer was measured. A result is collectively shown in Table 4.

[0150]

[Table 4]

[0151] The particle the number of particle which carries out adsorption survival on a thermal oxidation film wafer front face carries out [particle] adsorption survival on 30 and a copper deposition wafer front face is 5, and the nonionic surfactant which is a cleaning agent of this invention so that clearly from Table 4, and the cleaning agent (example 6) containing the fourth class ammonium are understood that the particle removal effectiveness is remarkably high also when it is any. On the other hand, the particle the number of particle which carries out adsorption survival on a thermal

oxidation film wafer front face carries out [particle] adsorption survival on 1200 and a copper deposition wafer front face is 202, and a cationic surfactant and the cleaning agent (example 6 of a comparison) containing the fourth class ammonium are understood that the particle removal effectiveness is low also when it is any.

[0152] The copper deposition wafer produced by the above-mentioned approach to the cleaning agent (pH11) which dissolved the diisobutyl dimethyl butynediol polyoxy-ethylene-glycol ether whose number of average mols of an oxyethylene radical [p+p'] is 4 0.05% in the above-mentioned general formula [6] which are 3% and a nonionic surface active agent about ammonia was immersed for 30 minutes at the room temperature (25 degrees C) into example 7 ultrapure water. Then, a wafer is pulled up, with ultrapure water, the rinse was carried out for 10 minutes and spin desiccation was carried out.

[0153] Diisobutyl dimethyl butynediol polyoxypropylene glycol ether whose number of average mols of an oxypropylene radical [q+q'] diethanolamine is indicated to be 3% in example 8 ultrapure water by the following general formula [8] which is a nonionic surfactant, and is 4 [0154]

[Formula 51]

[0155] The copper deposition wafer was processed by the same approach as an example 7 except having used the cleaning agent (pH10) which dissolved 0.05%.

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審査請求 未請求 請求項の数36 O L (全16頁) 最終頁に続く

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最終頁に続く

(54) 【発明の名称】 銅配線半導体基板洗浄剤

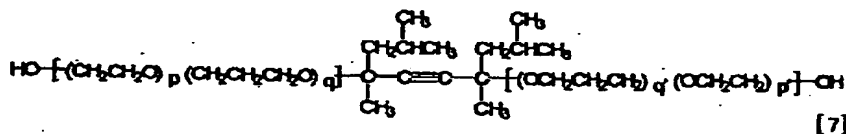
(57) 【要約】 (修正有)

【課題】 表面に銅配線が施された半導体表面を、銅配線の腐蝕や酸化を起こさず、且つ表面荒れを起こすことなく、当該表面の不純物を有効に除去し得る洗浄剤及び洗浄方法を提供する。

【解決手段】 分子中に



の基を有する、例えば一般式7のノニオン性界面活性剤を含む、表面に銅配線が施された半導体表面用の洗浄剤、これを用いた半導体表面の洗浄方法並びに該洗浄剤で処理して得た表面に銅配線が施された半導体。



(p + q + p' + q' は1 ~ 20である。)

【特許請求の範囲】

【請求項1】ノニオン性界面活性剤を含んでなる、表面に銅配線が施された半導体表面用洗浄剤。

【請求項2】ノニオン性界面活性剤が、分子中に

【化1】



で示される基を有するものである請求項1の何れかに記載の洗浄剤。

【請求項3】ノニオン性界面活性剤が、分子中に

【化2】

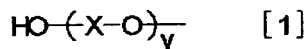


で示される基と、ポリオキシアルキレン基を有するものである請求項1の何れかに記載の洗浄剤。

【請求項4】ポリオキシアルキレン基が、下記一般式

【1】で示されるものである請求項3に記載の洗浄剤。

【化3】

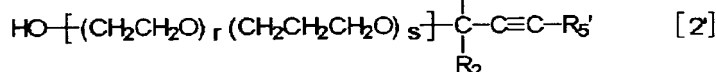


(式中、Xはアルキレン基を、yは正の整数を示す。)

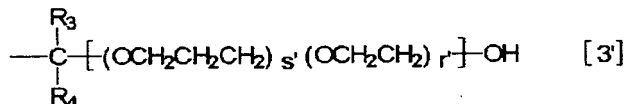
【請求項5】ポリオキシアルキレン基が、ポリオキシエチレン基又は／及びポリオキシプロピレン基である請求項3に記載の洗浄剤。

【請求項6】ノニオン性界面活性剤が、下記一般式

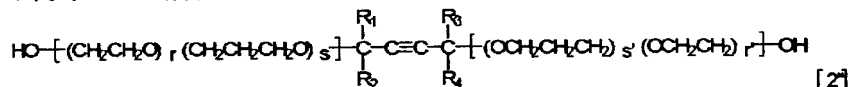
【2】で示されるものである請求項1に記載の洗浄剤。



(式中、R₁及びR₂は夫々独立して水素原子、水酸基、アルキル基又はヒドロキシアルキル基を示し、r及びsは夫々独立して0又は正の整数を示し、R₅'は水素原

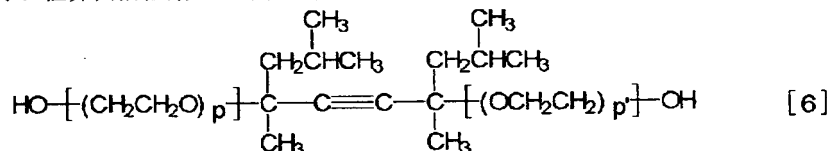


(式中、R₃及びR₄は夫々独立して水素原子、水酸基、アルキル基又はヒドロキシアルキル基を示し、r'及びs'は夫々独立して0又は正の整数を示す。)但し、r、s、r'及びs'が同時に0の場合を除く。)



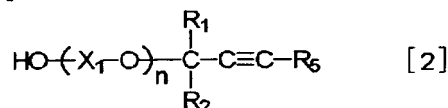
(式中、R₁、R₂、R₃、R₄、r、r'、s及びs'は前記と同じ。)

【請求項10】ノニオン性界面活性剤が、下記一般式



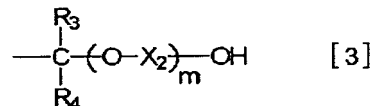
(式中、p+p'は1~20である。)

【化4】



(式中、X₁は低級アルキレン基を示し、nは正の整数を示し、R₁及びR₂は夫々独立して水素原子、水酸基、アルキル基又はヒドロキシアルキル基を示し、R₅は水素原子、水酸基、アルキル基、ヒドロキシアルキル基又は下記一般式【3】で示される基を示す。

10 【化5】



(式中、R₃及びR₄は夫々独立して水素原子、水酸基、アルキル基又はヒドロキシアルキル基を示し、X₂は低級アルキレン基を示し、mは正の整数を示す。)

【請求項7】一般式【2】に於いて、R₅が一般式【3】で示される基であり、n個のX₁及びm個のX₂は夫々独立してエチレン基又はプロピレン基である請求項6に記載の洗浄剤。

【請求項8】ノニオン性界面活性剤が、下記一般式【2'】で示されるものである請求項1に記載の洗浄剤。

【化6】

子、水酸基、アルキル基、ヒドロキシアルキル基又は下記一般式【3'】で示される基を示す。

30 【化7】

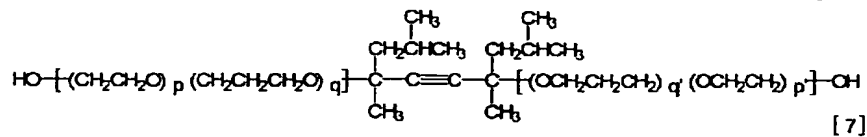
【請求項9】ノニオン性界面活性剤が、下記一般式【2''】で示されるものである請求項1に記載の洗浄剤。

【化8】

【6】、【7】又は【8】で示される化合物から選ばれるものである請求項1に記載の洗浄剤。

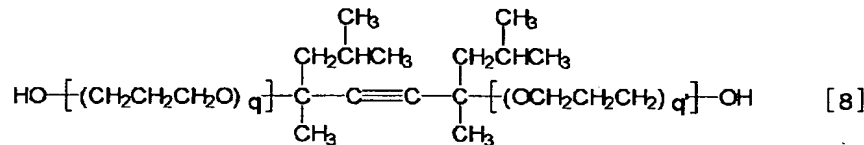
【化9】

【化10】



(式中、 $p+q+p'+q'$ は1~20である。)

【化11】



(式中、 $q+q'$ は1~20である。)

10 を示す。)

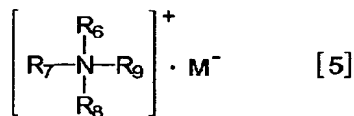
【請求項11】アルカリ性である請求項1~10の何れかに記載の洗浄剤。

【請求項12】更に含窒素アルカリ性化合物を含んでなる請求項1~11の何れかに記載の洗浄剤。

【請求項13】含窒素アルカリ性化合物がアンモニア、一級アミン、二級アミン、三級アミン又は四級アンモニウムから選ばれたものである請求項12に記載の洗浄剤。

【請求項14】四級アンモニウムが、下記一般式〔5〕で示される四級アンモニウムである請求項13に記載の 20 洗浄剤。

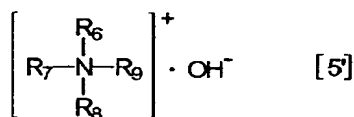
【化12】



(式中、 $\text{R}_6 \sim \text{R}_9$ は夫々独立して水酸基を有していてもよい炭化水素残基を示し、 M^- はアニオンを示す。)

【請求項15】一般式〔5〕で示される四級アンモニウムが下記一般式〔5'〕で示されるものである請求項1 30 4に記載の洗浄剤。

【化13】

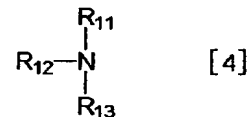


(式中、 $\text{R}_6 \sim \text{R}_9$ は夫々独立して炭素数1~6の低級アルキル基又は炭素数1~6のヒドロキシ低級アルキル基

【請求項16】一般式〔5〕で示される四級アンモニウムが、水酸化テトラメチルアンモニウム又は水酸化トリメチル-2-ヒドロキシエチルアンモニウムである請求項15に記載の洗浄剤。

【請求項17】アンモニア、一級アミン、二級アミン又は三級アミンが下記一般式〔4〕で示されるものである請求項13に記載の洗浄剤。

【化14】



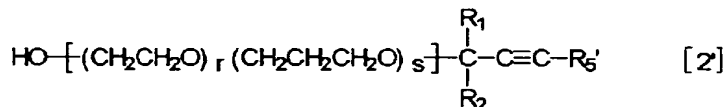
(式中、 R_{11} 、 R_{12} 及び R_{13} は、夫々独立して水素原子、低級アルキル基、又はヒドロキシ低級アルキル基を示す。)

【請求項18】表面に銅配線が施された半導体表面を、請求項1~17の何れかに記載の洗浄剤で処理することを特徴とする、表面に銅配線が施された半導体表面の洗浄方法。

【請求項19】表面に銅配線が施された半導体表面を、請求項1~17の何れかに記載の洗浄剤の存在下、物理的洗浄工程に付すことを特徴とする半導体表面の洗浄方法。

【請求項20】請求項18又は19に記載の方法によって表面に銅配線が施された半導体表面を洗浄することにより得られた表面に銅配線が施された半導体。

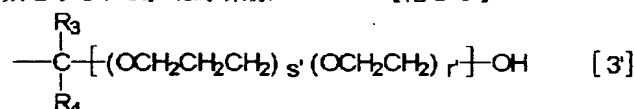
【請求項21】下記一般式〔2'〕で示される化合物 【化15】



(式中、 R_1 及び R_2 は夫々独立して水素原子、水酸基、アルキル基又はヒドロキシアルキル基を示し、 r 及び s は夫々独立して0又は正の整数を示し、 R_5' は水素原

子、水酸基、アルキル基、ヒドロキシアルキル基又は下記一般式〔3'〕で示される基を示す。

【化16】



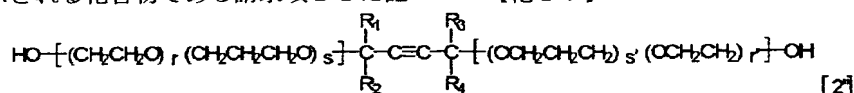
(式中、 R_3 及び R_4 は夫々独立して水素原子、水酸基、アルキル基又はヒドロキシアルキル基を示し、 r' 及び s' は夫々独立して0又は正の整数を示す。)

但し、 r 、 s 、 r' 及び s' が同時に0の場合を除く。)と含窒素アルカリ性化合物とを含んでなる半導体基板洗浄剤。

【請求項22】一般式〔2'〕で示される化合物が下記一般式〔2''〕で示される化合物である請求項21に記

載の洗浄剤。

【化17】



(式中、 R_1 、 R_2 、 R_3 、 R_4 、 r 、 r' 、 s 及び s' は前記と同じ。)

【請求項23】一般式〔2''〕に於いて、 R_1 及び R_3 がメチル基であって、 R_2 及び R_4 がイソブチル基である請求項22に記載の洗浄剤。

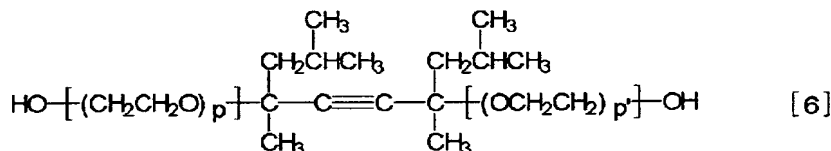
【請求項24】一般式〔2''〕に於いて、 r 、 r' 、 s 及び s' の総数が1~20である請求項22又は23に記載の洗浄剤。

【請求項25】一般式〔2''〕に於いて、 r 、 r' 、 s 及び s' の総数が1~18である請求項22又は23に記載の洗浄剤。

【請求項26】一般式〔2''〕で示される化合物が下記一般式〔6〕、〔7〕又は〔8〕で示される化合物から

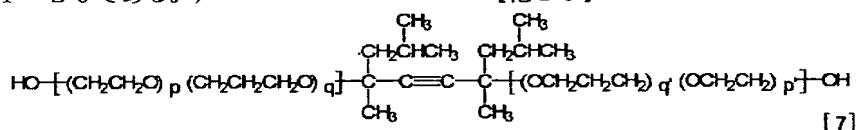
選ばれるものである請求項22に記載の洗浄剤。

【化18】



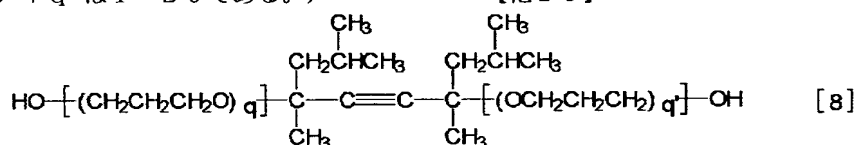
(式中、 $p+p'$ は1~20である。)

【化19】



(式中、 $p+q+p'+q'$ は1~20である。)

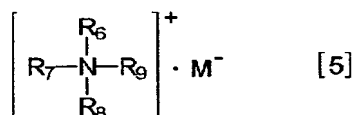
【化20】



(式中、 $q+q'$ は1~20である。)

【請求項27】含窒素アルカリ性化合物がアンモニア、一級アミン、二級アミン、三級アミン又は下記一般式〔5〕で示される四級アンモニウムから選ばれたものである請求項21~26の何れかに記載の洗浄剤。

【化21】

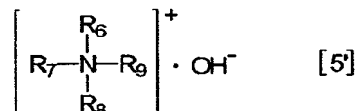


(式中、 $\text{R}_6 \sim \text{R}_9$ は夫々独立して水酸基を有していてもよい炭化水素残基を示し、 M^- はアニオンを示す。)

【請求項28】含窒素アルカリ性化合物が一般式〔5〕で示される四級アンモニウムである請求項21~26の何れかに記載の洗浄剤。

【請求項29】一般式〔5〕で示される四級アンモニウムが下記一般式〔5'〕で示されるものである請求項28に記載の洗浄剤。

【化22】



(式中、 $\text{R}_6 \sim \text{R}_9$ は夫々独立して炭素数1~6の低級アルキル基又は炭素数1~6のヒドロキシ低級アルキル基を示す。)

【請求項30】一般式〔5〕又は〔5'〕に於いて、 $\text{R}_6 \sim \text{R}_9$ で示される炭化水素残基がアルキル基である請求項28又は29に記載の洗浄剤。

【請求項31】 $\text{R}_6 \sim \text{R}_9$ で示されるアルキル基がメチル基である請求項30に記載の洗浄剤。

【請求項32】一般式〔5'〕で示される四級アンモニウムが水酸化テトラメチルアンモニウム又は水酸化トリメチル-2-ヒドロキシエチルアンモニウムである請求項29に記載の洗浄剤。

【請求項33】半導体基板が、表面に銅配線が施された半導体基板である請求項21~32の何れかに記載の洗浄剤。

【請求項34】請求項21~32の何れかに記載の洗浄剤で半導体表面を処理することを特徴とする半導体基板洗浄方法。

【請求項35】半導体基板が、表面に銅配線が施された半導体基板である請求項34に記載の洗浄方法。

【請求項36】請求項34又は35に記載の方法で半導体表面を洗浄することによって得られた半導体基板。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、半導体表面、特に、表面に銅配線が施された半導体表面の洗浄剤及び洗浄方法に関する。

【0002】

【従来の技術】近年、LSIの構造は、高集積化に伴い微細化が進んでおり、半導体表面に金属配線などが幾段にも重ねられた多層構造となっている。また、使用される配線も従来のアルミニウムから、より電気的抵抗の低い銅(Cu)への変更が提案されている。

【0003】表面に銅配線が多層に亘って施された多層構造を有する半導体を製造する工程には、金属Cuを酸化しながら物理的に半導体基板を研磨して平坦化するいわゆる化学的物理的研磨技術(Cu-CMP)が利用される。

【0004】一方、Cu-CMP工程後の半導体表面には、Cu配線とそれぞれのCu配線を隔離する絶縁膜(酸化ケイ素)が剥き出しの状態となっており、Cu-CMP工程後のウエハー表面は多量の不純物金属とパーティクルとにより汚染されている。不純物金属汚染はCMPによって削り取られるCuが絶縁膜上の吸着し酸化銅として残存することに起因しており、また、パーティクル汚染はCMP工程で研磨のために用いられるスラリーに由来している。

【0005】このように絶縁膜上に酸化銅が残存すると、後工程での熱処理で銅元素が絶縁膜中に拡散し、絶縁性が低下することでデバイスの特性が劣化してしまい、汚染が著しい場合は、隔離した配線同士が結線、即ち、ショートを起こしてしまうため、デバイスが破壊されてしまう。そのため、次工程に進む前に、酸化銅を除去する必要がある。また、パーティクル汚染も同様に次工程に悪影響を及ぼすため、極力除去する必要がある。

【0006】以上の理由で、上記した如き不純物やパーティクルを除去するために、Cu-CMP工程後の洗浄工程は必須である。

【0007】Cu-CMP工程後の洗浄工程に於いて、従来、半導体用の洗浄液として通常用いられている酸性の洗浄液(塩酸やフッ酸など)を用いると、絶縁膜上に付着した酸化銅のみならず、配線の金属銅をも溶解してしまい、配線の腐蝕や断線を引き起こすため、当該酸性洗浄液の使用は好ましくない。更に、酸性の溶液を用いると、半導体表面とパーティクルとが静電的に引き合い、パーティクルが除去できないばかりでなく逆吸着を引き起こしてしまうという問題もある。また、パーティクルの除去には半導体表面とパーティクルとが静電的に反発し合うアルカリ性の洗浄液が一般に有効であるとされているが、アルカリ源として金属イオンを含んだ水酸化ナ

トリウムや水酸化カリウム等の洗浄液を用いた場合には、これらの金属が絶縁膜(酸化ケイ素)表面に吸着し、絶縁特性を劣化させてしまう。またアルカリ性の洗浄液のうち、金属イオンを含まない無機アルカリ(アンモニア水等)の洗浄液は、銅の溶解力が強く使用できない。

【0008】一方、四級アンモニウムを含む洗浄液は、銅配線を腐蝕することではなく、パーティクルの除去効果も高いという利点があるものの、四級アンモニウムは強アルカリ性であるため、絶縁膜に対するエッチング力が強く、CMP工程で平坦化した表面を荒らしてしまうという欠点を有している。このような欠点を解消するために四級アンモニウムに過酸化水素を添加することにより、エッチング速度を遅くすることが可能であることが知られている。しかしながら、この場合、過酸化水素の酸化力により、銅配線の表面が酸化し、導電性が悪くなってしまうという問題が生じる。

【0009】この様に、銅配線を施した半導体基板を、銅配線の腐蝕や酸化を起こさず、かつ、表面荒れを起こすことなく、表面の不純物を除去できる洗浄液は、これまで存在しなかった。

【0010】

【発明が解決しようとする課題】本発明は、上記した如き状況に鑑みなされたもので、半導体表面、特に、表面に銅配線が施された半導体表面を、銅配線の腐蝕や酸化を起こさず、且つ表面荒れを起こすことなく、当該表面の不純物を有効に除去し得る洗浄剤及び洗浄方法を提供するものである。

【0011】

【課題を解決するための手段】本発明は、以下の構成よりなる。

【0012】(1)ノニオン性界面活性剤を含んでなる、表面に銅配線が施された半導体表面用洗浄剤。

【0013】(2)表面に銅配線が施された半導体表面を、ノニオン性界面活性剤を含んでなる洗浄剤で処理することを特徴とする、表面に銅配線が施された半導体表面の洗浄方法。

【0014】(3)表面に銅配線が施された半導体表面をノニオン性界面活性剤を含んでなる洗浄剤で処理することによって得られた、表面に銅配線が施された半導体。

【0015】本発明者等は上記目的を達成すべく鋭意研究を重ねた結果、ノニオン性界面活性剤を含有する洗浄剤を用いて、銅配線が施された半導体表面を洗浄することにより、絶縁膜のエッチング速度をコントロールでき、銅配線の腐食や酸化を起こさず、且つ表面荒れを起こすことなく、絶縁膜や銅配線上に吸着している酸化銅やパーティクルのような不純物を有効に除去し得ること、更にこのような効果はノニオン性界面活性剤として、その分子中に

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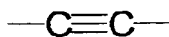
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【0016】

【化23】



【0017】で示されるアセチレン基を有するものが特に好ましいこと並びにこのような界面活性剤と、例えばアンモニア、一級乃至三級アミン又は四級アンモニウム等の含窒素アルカリ性化合物、なかでも特に四級アンモニウムとを併用することにより、その効果がより一層助長されることを見出し、これら一連の発見に基づいて本発明を完成させるに至った。

【0018】本発明に於けるノニオン性界面活性剤としては、従来より知られているものが何れも用いられるが、その分子中に

【0019】

【化24】



【0020】で示される基（アセチレン基）を有するものが好ましく、特に分子中に

【0021】

【化25】

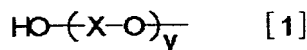


【0022】で示される基（アセチレン基）とポリオキシアルキレン基を有するものが好ましい。

【0023】当該ポリオキシアルキレン基としては、例えば下記一般式〔1〕で示されるものが挙げられる。

【0024】

【化26】



【0025】（式中、Xはアルキレン基を、yは正の整数を示す）。

【0026】一般式〔1〕に於いて、Xで示されるアルキレン基としては、例えば直鎖状、分枝状あるいは環状の炭素数1～6の低級アルキレン基が好ましく、例えばメチレン基、エチレン基、プロピレン基、ブチレン基、メチルメチレン基、エチルエチレン基、メチルエチレン基、メチルプロピレン基、エチルプロピレン基、ペンチレン基、ヘキシレン基、シクロペンチレン基、シクロヘキシレン基等が挙げられ、なかでもエチレン基又はプロピレン基等が特に好ましい。また、yは正の整数を示し、通常1～10、好ましくは1～8であり、なかでもyが2～8のものは、気泡性が低く、物理的洗浄と併用した場合にも泡立ちが抑えられ、泡によるトラブルが発生しにくい、特に好ましい。尚、y個のオキシアルキレン基は、すべて同一でもよいし、二種又はそれ以上からなってもよい。一般式〔1〕に於いて—(X—O)—で示されるオキシアルキレン基のなかでは、例えばオキシエチレン基、オキシプロピレン基等が好ましく、—(X—O)—_y—で示されるポリオキシアルキレン基としては、例えばオキシエチレン基のみからなるもの、

の、オキシプロピレン基のみからなるもの、オキシエチレン基とオキシプロピレン基の組み合わせからなるもの等が特に好ましい。尚、オキシエチレン基とオキシプロピレン基の組み合わせとからなるものである場合、両者の比率は通常オキシエチレン基が50%以上、好ましくは70%以上である。

【0027】上記した如き、分子中に、

【0028】

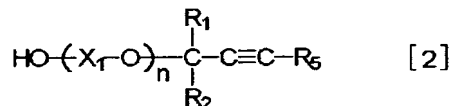
【化27】



【0029】で示される基と、前記一般式〔1〕で示されるポリオキシアルキレン基を有するノニオン性界面活性剤の具体例としては、例えば下記一般式〔2〕で示されるもの等が挙げられる。

【0030】

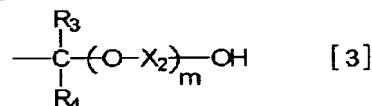
【化28】



20 【0031】（式中、X₁は低級アルキレン基を示し、nは正の整数を示し、R₁及びR₂は夫々独立して水素原子、水酸基、アルキル基又はヒドロキシアルキル基を示し、R₅は水素原子、水酸基、アルキル基、ヒドロキシアルキル基又は下記一般式〔3〕で示される基を示す。

【0032】

【化29】



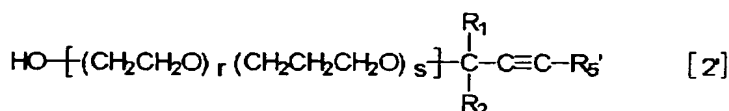
30 【0033】（式中、R₃及びR₄は夫々独立して水素原子、水酸基、アルキル基又はヒドロキシアルキル基を示し、X₂は低級アルキレン基を示し、mは正の整数を示す。）

40 【0034】上記一般式〔2〕及び〔3〕に於いてX₁及びX₂で示される低級アルキレン基は、前述した如き一般式〔1〕に於けるXと同じである。また、m及びnも同じく前述した如き一般式〔1〕に於けるyと同じである。尚、一般式〔2〕に於けるR₅が一般式〔3〕である場合は、mとnの合計は、通常2～20、好ましくは2～16であり、なかでも4～16のものは、気泡性が低く、物理的洗浄と併用した場合にも泡立ちが抑えられ、泡によるトラブルが発生しにくい、特に好ましい。

【0035】上記した如き一般式〔2〕で示されるノニオン性界面活性剤のなかでも、X₁及びX₂がエチレン基又は/及びプロピレン基であるものが好ましい。これら好ましいものとしては、例えば下記一般式〔2'〕で示されるものが挙げられる。

【0036】

【化30】

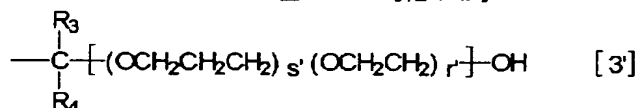


【0037】〔式中、 R_1 及び R_2 は前記と同じであり、 r 及び s は夫々独立して0又は正の整数を示し、 R_5' は水素原子、水酸基、アルキル基、ヒドロキシアルキル基

又は下記一般式〔3'〕で示される基を示す。

【0038】

〔化31〕



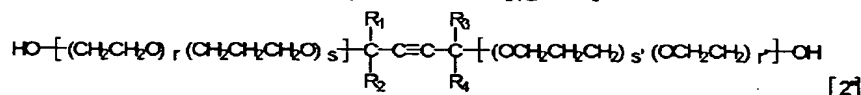
【0039】〔式中、 R_3 及び R_4 は前記と同じであり、 r' 及び s' は夫々独立して0又は正の整数を示す。〕但し、 r 、 s 、 r' 及び s' が同時に0の場合を除く。〕

10 示される基が一般式〔3'〕であるもの、即ち、下記一般式〔2'〕で示されるものが特に好ましい。

【0041】

〔化32〕

【0040】なかでも、一般式〔2'〕に於いて R_5' で



【0042】〔式中、 R_1 、 R_2 、 R_3 、 R_4 、 R_5 、 r 、 r' 、 s 及び s' は前記と同じ。〕

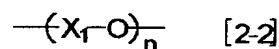
ンオキサイドとを反応させればよい。

【0051】

〔化36〕

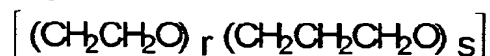
【0043】尚、上記一般式〔2'〕及び〔2''〕に於いて、

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【0044】

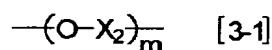
〔化33〕



【0052】及び

【0053】

〔化37〕



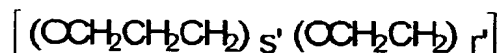
【0045】は、 r 個のオキシエチレン基のブロックと s 個のオキシプロピレン基のブロックからなるもの（いわゆるブロック共重合体）及びオキシエチレン基とオキシプロピレン基とが順不同に結合し、前者の総数が r 個で後者の総数が s 個であるもの（いわゆるランダム共重合体）を意味する。また、上記一般式〔3'〕及び〔2''〕に於ける

【0054】〔式中、 X_1 、 X_2 、 n 及び m は前記と同じ。〕

【0055】上記式〔2〕、〔3〕、〔2'〕、〔3'〕及び〔2''〕に於いて、 $\text{R}_1 \sim \text{R}_5$ 及び R_5' で示されるアルキル基としては、飽和でも不飽和でもよく、直鎖状、分枝状或いは環状の炭素数1~10、好ましくは1~6、更に好ましくは1~3である。具体的には、例えばメチル基、エチル基、 n -プロピル基、 n -ブチル基、 n -ペンチル基、 n -ヘキシル基、 n -オクチル基、 n -ノニル基、 n -デカニル基等の飽和直鎖アルキル基、例えばiso-プロピル基、iso-ブチル基、sec-ブチル基、tert-ブチル基、iso-ペンチル基、sec-ペンチル基、tert-ペンチル基、ネオペンチル基、iso-ヘキシル基、sec-ヘキシル基、tert-ヘキシル基等の飽和分枝アルキル基、例えばシクロペンチル基、シクロヘキシル基等の環状アルキル基、例えばビニル基、 n -プロベニル基、 n -ブテニル基等の不飽和直鎖アルキル基、例えばiso-プロベニル基、iso-ブテニル基、sec-ブテニル基、tert-ブテニル基等の不飽和分枝アルキル基が挙げられる。ヒドロキシアルキル基としては、これらアルキル基の任意の水素原子のうち1又はそれ以上、好ましくは1~3、より好ましくはその末端の水素原子のみが水酸基で置換されたもの等が挙げられる。

【0046】

〔化34〕

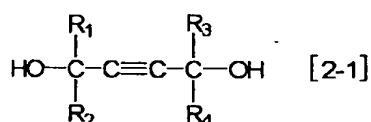


【0047】も同様である。

【0048】本発明に係るノニオン性界面活性剤は自他公知の方法により容易に調製し得る。即ち、例えば、一般式〔2〕に於いて R_5 で示される基が一般式〔3〕である化合物を調製するには、例えば米国特許第3291607号に記載の方法に従い、下記一般式〔2-1〕で示されるグリコール化合物と、

【0049】

〔化35〕



【0050】〔式中、 $\text{R}_1 \sim \text{R}_4$ は前記と同じ。〕下記一般式〔2-2〕又は〔3-1〕に対応するアルキレ

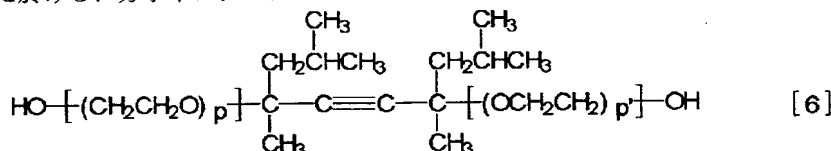
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【0056】尚、 r 、 s 、 r' 及び s' の合計は、通常1

13

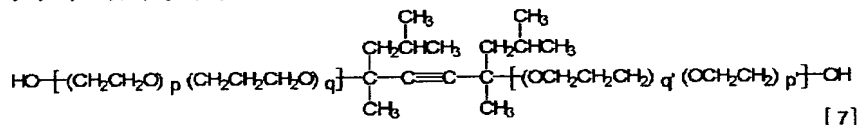
～20、好ましくは1～16であり、特に4～16のものは、気泡性が低く、物理的洗浄と併用した場合にも泡立ちが抑えられ、泡によるトラブルが発生しにくい、特に好ましい。なかでも、s及びs'が夫々独立して0～2であって、r及びr'が夫々独立して4～6であるものがより好ましい。

【0057】本発明に於ける、分子中にアセチレン基を



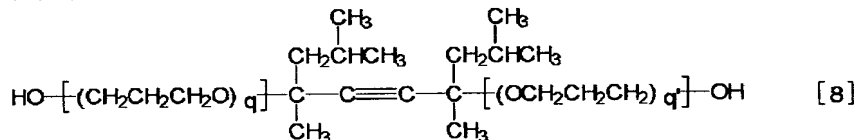
【0059】〔式中、pとp'の総数(p+p')は、通常1～20、好ましくは1～16、より好ましくは4～16である。〕、

【0060】例えば下記一般式〔7〕で示されるジイソブチルジメチルブチンジオールポリオキシエチレン/ポ



【0062】〔式中、p、q、p'及びq'の総数(p+q+p'+q')は、通常1～20、好ましくは1～16、より好ましくは4～16である。〕、

【0063】例えば下記一般式〔8〕で示されるジイソブチルジメチルブチンジオールポリオキシプロピレング



【0065】〔式中、qとq'の総数(q+q')は、通常1～20、好ましくは1～16、より好ましくは4～16である。〕等が挙げられる。

【0066】本発明に於いて用いられるノニオン性界面活性剤は、前述した如き方法によって調製されたものでも市販品でも、いずれでもよい。上記した如きノニオン性界面活性剤は、単独で使用しても、また、2種以上適宜組み合わせ用いてもよい。

【0067】ノニオン性界面活性剤の使用量は、臨界ミセル濃度以上であればよく、それより薄ければエッチングの速度が速くなり、効果が薄れる。具体的な使用量としては、界面活性剤の種類により異なるため一概には言えないが、例えば通常1ppm以上であり、特に上限はない。但し、経済性等を考慮すると、1～10000ppmが好ましく、より好ましくは10～1000ppmである。

【0068】本発明に於けるアンモニア、一級乃至三級アミンとしては、例えば下記一般式〔4〕で示されるもの等が挙げられる。

【0069】

〔化41〕

14

有するノニオン性界面活性剤の具体例としては、例えば下記一般式〔6〕で示されるジイソブチルジメチルブチンジオールポリオキシエチレングリコールエーテル (1,4-diisobutyl-1,4-dimethylbut-2-yn diol polyoxyethylene glycol ether)

【0058】

〔化38〕

リオキシプロピレングリコールエーテル (1,4-diisobutyl-1,4-dimethylbut-2-yn diol polyoxypropylene glycol ether)

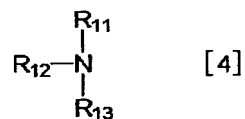
【0061】

〔化39〕

リコールエーテル (1,4-diisobutyl-1,4-dimethylbut-2-yn diol polyoxypropylene glycol ether)

【0064】

〔化40〕



【0070】〔式中、R₁₁、R₁₂及びR₁₃は、夫々独立して水素原子、低級アルキル基、又はヒドロキシ低級アルキル基を示す。〕

【0071】一般式〔4〕に於いてR₁₁～R₁₃で示される低級アルキル基としては、例えば直鎖状、分枝状あるいは環状の炭素数1～6のものが挙げられ、具体的には、例えばメチル基、エチル基、n-プロピル基、iso-プロピル基、n-ブチル基、iso-ブチル基、sec-ブチル基、tert-ブチル基、n-ペンチル基、iso-ペンチル基、sec-ペンチル基、tert-ペンチル基、ネオペンチル基、n-ヘキシル基、iso-ヘキシル基、sec-ヘキシル基、tert-ヘキシル基、シクロペンチル基、シクロヘキシル基等が挙げられる。一般式〔4〕に於いてR₁₁～R₁₃で示されるヒドロキシ低級アルキル基としては、上記した如き低級アルキル基の任意の水素原子のうち1又はそれ以上、好ましくはその末端の水素原子が水酸基で置換されたもの

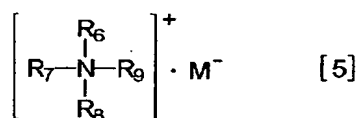
が挙げられ、具体的には、例えばヒドロキシメチル基、ヒドロキシエチル基、3-ヒドロキシ-n-プロピル基、4-ヒドロキシ-n-ブチル基、1-メチル-2-ヒドロキシエチル基、2-メチル-3-ヒドロキシプロピル基、1,1-ジメチル-2-ヒドロキシエチル基等が挙げられる。

【0072】一般式〔4〕で示される化合物の具体例としては例えばアンモニア、例えばメチルアミン、エチルアミン、n-プロピルアミン、n-ブチルアミン等の一級アミン、例えばジメチルアミン、ジエチルアミン、メチルエチルアミン、ジ-n-プロピルアミン、ジ-n-ブチルアミン等の二級アミン、例えばトリメチルアミン、トリエチルアミン、メチルジエチルアミン、トリ-n-プロピルアミン、トリ-n-ブチルアミン等の三級アミン、例えばモノエタノールアミン等の一級ヒドロキシアミン、例えばジエタノールアミン等の二級ヒドロキシアミン、例えばトリエタノールアミン等の三級ヒドロキシアミン等が挙げられる。

【0073】本発明に於ける四級アンモニウムとしては、例えば下記一般式〔5〕で示されるもの等が挙げられる。

【0074】

〔化42〕



【0075】(式中、 $R_6 \sim R_9$ は夫々独立して水酸基を有していてもよい炭化水素残基を示し、 M^- はアニオンを示す。)

【0076】一般式〔5〕に於いて $R_6 \sim R_9$ で示される水酸基を有していてもよい炭化水素残基の炭化水素残基としては、脂肪族、芳香族、芳香脂肪族、或いは脂環族の何れでもよく、また、脂肪族及び芳香脂肪族に於ける脂肪族としては、飽和でも不飽和でも、また、直鎖状でも分枝状でもよい。これらのうちの代表的なものとしては、例えば直鎖状、分枝状、或いは環状の飽和又は不飽和のアルキル基、アラキル基、アリール基等が挙げられる。アルキル基としては、通常炭素数が1~6の低級アルキル基、特に炭素数1~4の低級アルキル基が好ましく、具体的には、例えばメチル基、エチル基、n-プロピル基、iso-プロピル基、n-ブチル基、iso-ブチル基、sec-ブチル基、tert-ブチル基、n-ペンチル基、iso-ペンチル基、sec-ペンチル基、tert-ペンチル基、ネオペンチル基、n-ヘキシル基、iso-ヘキシル基、sec-ヘキシル基、tert-ヘキシル基、シクロペンチル基、シクロヘキシル基、ビニル基、n-プロベニル基、iso-プロベニル基、n-ブテニル基、iso-ブテニル基、sec-ブテニル基、tert-ブテニル基等が挙げられる。アラキル基としては、通常炭素数7~12のものが挙げられ、具体的に、例えばベンジル基、フェネチル基、フェニルプロピ

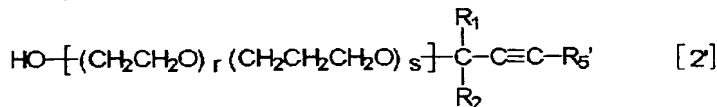
ル基、フェニルブチル基、フェニルヘキシル基、メチルベンジル基、メチルフェネチル基、エチルベンジル基等が挙げられる。アリール基としては、通常炭素数6~14のものが挙げられ、具体的には、例えばフェニル基、o-トリル基、m-トリル基、p-トリル基、2,3-キシリル基、2,4-キシリル基、2,5-キシリル基、2,6-キシリル基、3,5-キシリル基、ナフチル基、アントリル基等が挙げられる。尚、上記した如きアリール基又はアラキル基の芳香環には、例えばメチル基、エチル基等の低級アルキル基や、ハロゲン原子、ニトロ基、アミノ基等を置換基として有していてもよい。水酸基を有する炭化水素残基としては、上記した炭化水素残基の水素原子が水酸基で置換されたものが挙げられる。一般式〔5〕に於いて M^- で示されるアニオンとしては、例えば OH^- 等が挙げられる。

【0077】上記した如き四級アンモニウムの具体例としては、例えば以下のものが挙げられる。水酸化テトラメチルアンモニウム(TMAH)、水酸化トリメチル-2-ヒドロキシエチルアンモニウム(コリン)、水酸化テトラエチルアンモニウム、水酸化テトラプロピルアンモニウム、水酸化テトラブチルアンモニウム、水酸化モノメチルトリエチルアンモニウム、水酸化ジメチルジエチルアンモニウム、水酸化トリメチルモノエチルアンモニウム、水酸化モノメチルトリプロピルアンモニウム、水酸化ジメチルジプロピルアンモニウム、水酸化トリメチルモノプロピルアンモニウム、水酸化モノメチルトリブチルアンモニウム、水酸化ジメチルジブチルアンモニウム、水酸化トリメチルモノブチルアンモニウム、水酸化モノエチルトリプロピルアンモニウム、水酸化ジエチルジプロピルアンモニウム、水酸化トリエチルモノプロピルアンモニウム、水酸化モノエチルトリブチルアンモニウム、水酸化ジエチルジブチルアンモニウム、水酸化トリエチルモノブチルアンモニウム、水酸化モノプロピルトリブチルアンモニウム、水酸化ジプロピルジブチルアンモニウム、水酸化トリプロピルモノブチルアンモニウム、水酸化トリエチル-2-ヒドロキシエチルアンモニウム、水酸化トリプロピル-2-ヒドロキシエチルアンモニウム、水酸化トリブチル-2-ヒドロキシエチルアンモニウム、水酸化トリメチル-3-ヒドロキシプロピルアンモニウム、水酸化トリエチル-3-ヒドロキシプロピルアンモニウム、水酸化トリプロピル-3-ヒドロキシプロピルアンモニウム、水酸化トリブチル-3-ヒドロキシプロピルアンモニウム、水酸化トリメチル-4-ヒドロキシブチルアンモニウム、水酸化トリエチル-4-ヒドロキシブチルアンモニウム、水酸化トリプロピル-4-ヒドロキシブチルアンモニウム、水酸化トリブチル-4-ヒドロキシブチルアンモニウム、水酸化トリメチル-3-ヒドロキシブチルアンモニウム、水酸化トリエチル-3-ヒドロキシブチルアンモニウム、水酸化トリプロピル-3-ヒドロキシブチルアンモニウム、水酸化トリブチル-3-ヒドロキシ

ブチルアンモニウム、水酸化ジメチルエチル-2-ヒドロキシエチルアンモニウム、水酸化メチルジエチル-2-ヒドロキシエチルアンモニウム、水酸化ジメチルエチル-3-ヒドロキシプロピルアンモニウム、水酸化メチルジエチル-3-ヒドロキシプロピルアンモニウム、水酸化ジメチルエチル-4-ヒドロキシブチルアンモニウム、水酸化メチルジエチル-4-ヒドロキシブチルアンモニウム、水酸化ジメチルエチル-3-ヒドロキシブチルアンモニウム、水酸化メチルジエチル-3-ヒドロキシブチルアンモニウム、水酸化ジメチルジ(2-ヒドロキシエチル)アンモニウム、水酸化ジメチルジ(3-ヒドロキシプロピル)アンモニウム、水酸化ジメチルジ(3-ヒドロキシブチル)アンモニウム、水酸化ジメチルジ(4-ヒドロキシブチル)アンモニウム、水酸化ジエチルジ(2-ヒドロキシエチル)アンモニウム、水酸化ジエチルジ(3-ヒドロキシプロピル)アンモニウム、水酸化ジエチルジ(3-ヒドロキシブチル)アンモニウム、水酸化ジエチルジ(4-ヒドロキシブチル)アンモニウム、水酸化メチルエチルジ(2-ヒドロキシエチル)アンモニウム、水酸化メチルエチルジ(3-ヒドロキシプロピル)アンモニウム、水酸化ジエチルジ(3-ヒドロキシブチル)アンモニウム、水酸化メチルエチルジ(4-ヒドロキシブチル)アンモニウム、水酸化エチルトリ(2-ヒドロキシエチル)アンモニウム、水酸化エチルトリ(2-ヒドロキシエチル)アンモニウム、水酸化プロピルトリ(2-ヒドロキシエチル)アンモニウム、水酸化ブチルトリ(2-ヒドロキシエチル)アンモニウム、水酸化メチルトリ(3-ヒドロキシプロピル)アンモニウム、水酸化エチルトリ(3-ヒドロキシブチル)アンモニウム、水酸化メチルトリ(4-ヒドロキシブチル)アンモニウム、水酸化エチルトリ(4-ヒドロキシブチル)アンモニウム、水酸化メチルトリ(3-ヒドロキシブチル)アンモニウム、水酸化エチルトリ(3-ヒドロキシブチル)アンモニウム。これらの中でも、水酸化テトラメチルアンモニウム(TMAH)、水酸化トリメチル-2-ヒドロキシエチルアンモニウム(コリン)等が特に好ましい。

【0078】上記一般式〔4〕で示される化合物又は一般式〔5〕で示される四級アンモニウムは、単独で使用しても、また、2種以上適宜組み合わせ用いてもよい。

【0079】本発明に於いて用いられる一般式〔4〕で示される化合物又は一般式〔5〕で示される四級アンモニウムの使用量は、種類により異なるため一概には言え



【0089】(式中、 R_1 、 R_2 、 R_6 、 r 及び s は前記と同じ。)、主要成分としてなる半導体用洗浄剤。

【0090】(3)本発明の洗浄剤の更に好ましい態様としては、例えば以下の如きである。

(a')一般式〔5'〕で示される四級アンモニウムと

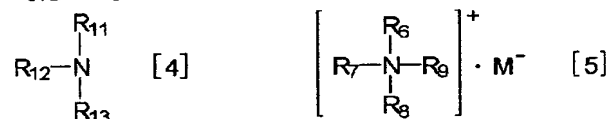
ないが、あまり低濃度ではエッチングの速度が遅くなり、効果が薄れるので、例えば通常0.003% (w/v)以上である。また、特に上限はないが、経済性等を考慮すると、0.003~10% (w/v)が好ましく、より好ましくは0.01~6% (w/v)、更に好ましくは0.05~1% (w/v)である。

【0080】(1)本発明の洗浄剤の好ましい態様としては、例えば以下のものが挙げられる。

(a)含窒素アルカリ性化合物として、一般式〔4〕で示されるアンモニア、一級乃至三級アミン又は一般式〔5〕で示される四級アンモニウムと

【0081】

〔化43〕

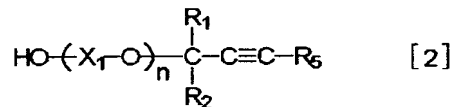


【0082】(式中、 R_6 、 R_7 、 R_8 、 R_9 、 R_{11} 、 R_{12} 、 R_{13} 及び M^- は前記と同じ。)、

(b)一般式〔2〕で示されるノニオン性界面活性剤と

【0083】

〔化44〕



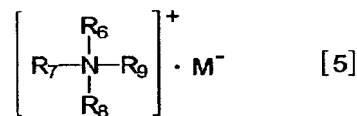
【0084】(式中、 R_1 、 R_2 、 R_6 、 X 及び n は前記と同じ。)、主要成分としてなる半導体用洗浄剤。

【0085】(2)本発明の洗浄剤のより好ましい態様としては、例えば以下の如きである。

(a')一般式〔5〕で示される四級アンモニウムと

【0086】

〔化45〕

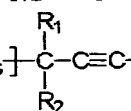


【0087】(式中、 R_6 、 R_7 、 R_8 、 R_9 及び M^- は前記と同じ。)、

(b')一般式〔2'〕で示されるノニオン性界面活性剤と

【0088】

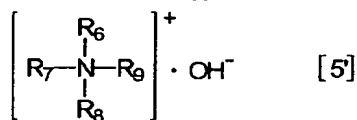
〔化46〕



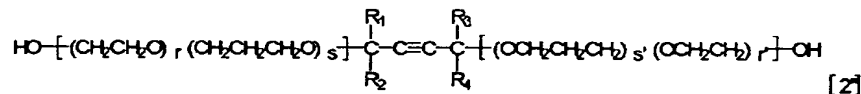
【0091】

〔化47〕

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【0092】(式中、 R_6 、 R_7 、 R_8 及び R_9 は前記と同



【0094】(式中、 R_1 、 R_2 、 R_3 、 R_4 、 r 、 s 、 r' 及び s' は前記と同じ。)、主要成分としてなる半導体用洗浄剤。

【0095】尚、上記態様に於いて、一般式[2']に於ける R_1 及び R_3 がメチル基、 R_2 及び R_4 がイソブチル基であって、一般式[5']に於ける $R_6 \sim R_9$ の全てがメチル基であるか、或いはそのうち3つがメチル基であって、残りの1つが2-ヒドロキシエチル基である場合が特に好ましい。

【0096】本発明の洗浄剤は、半導体のみならず、プリント基板やLCD基板等の洗浄剤としても使用し得るが、特に上記した如き態様は、表面に銅配線が施された半導体表面の洗浄に有用である。

【0097】本発明の洗浄剤は、通常水溶液の状態であり、上記した如きノニオン性界面活性剤、或いはノニオン性界面活性剤と含窒素アルカリ性化合物とを、水に添加溶解させることにより調製される。

【0098】このようにして調製した本発明の洗浄剤は、使用前に濾過処理等を行うのが好ましい。また、ここで用いられる水は、蒸留、イオン交換処理等により精製されたものであればよいが、この分野で用いられるいわゆる超純水がより好ましい。

【0099】本発明の洗浄剤は、アルカリ性が好ましく、通常pH9以上、好ましくはpH9~12、より好ましくはpH9.5~10.5である。このようなpH範囲とすることで、層間絶縁膜である SiO_2 をエッチングする恐れがより少なくなり、更には半導体表面とパーティクルとの電気的な反発が大きくなるので、パーティクル及びCuの洗浄効果が向上する。

【0100】本発明の洗浄剤を上記した如きpH範囲とするためには、要すれば、通常この分野で用いられるpH調整剤、例えばクエン酸、シュウ酸、フタル酸、酒石酸等のカルボン酸類、これらの誘導体、又はこれらの塩、リン酸、リン酸誘導体又は塩等を用いてもよい。

【0101】また、本発明の洗浄剤は、上記した如きpH範囲内に於いて緩衝能を有するものが特に好ましい。本発明の洗浄剤に緩衝能を付与するには、上記した如きpH調整剤のうち、それ自体が上記した如きpH範囲内で緩衝能を有するものを単独又は2種以上組み合わせても、或いはこれ以外のpH調整剤と組み合わせて用いてもよく、また、それ自体は緩衝能を有さないが、2種以上組み合わせて使用することにより本発明の洗浄剤に緩

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じ。)、

(b')一般式[2']で示されるノニオン性界面活性剤とを

【0093】

【化48】

衝能を付与し得るもの、或いは含窒素アルカリ性化合物と組み合わせて使用することにより本発明の洗浄剤に緩衝能を付与し得るものを用いてもよい。尚、上記した如き含窒素アルカリ性化合物のみで、本発明の洗浄剤に緩衝能を付与し得る場合は、特にpH調整剤を用いなくてもよいことは言うまでもない。

【0102】これらpH調整剤の使用量としては、使用するpH調整剤の種類により異なるため一概には言えないが、本発明の洗浄剤に添加させた際に、当該洗浄剤が上記した如きpH範囲内となるような量であればよく、例えば洗浄剤全量の通常0.0001~10% (w/v)、好ましくは0.001~1% (w/v) である。

【0103】また、本発明の洗浄剤中には、銅配線を溶解する能力を有さないキレート剤を添加してもよい。このようなキレート剤を添加することにより、液中に分散した酸化銅を可溶化し、再吸着を抑えることができ、また、CMP工程でのスラリー由来の不純物であるFeやAlなどを表面から除去することもできる。このような銅配線を溶解する能力を有さないキレート剤としては、例えばエチレンジアミン四酢酸(EDTA)、trans-1,2-ジアミノシクロヘキサン-N,N,N',N'-四酢酸(CyDTA)、ニトリロ三酢酸(NTA)等のカルボン酸類、例えばエチレンジアミンテトラキス(メチレンホスホン酸)(EDTP0)等のホスホン酸類が挙げられる。これらキレート剤の使用量としては、使用するキレート剤の種類により異なるため一概には言えないが、本発明の洗浄剤に添加させた際に、当該洗浄剤が上記した如き効果を奏し得るような量であればよく、例えば洗浄剤全量の通常0.0001~1% (w/v)、好ましくは0.001~0.1% (w/v) である。

【0104】更に、本発明の洗浄剤中には、上記した如きノニオン性界面活性剤と含窒素アルカリ性化合物との分離を抑える目的で、少量、例えば通常0.01~5% (w/v)、好ましくは0.1~1% (w/v) の有機溶剤を添加してもよい。有機溶剤としては、例えばメタノール、エタノール、イソプロピルアルコール、アセトン等が挙げられる。

【0105】本発明の洗浄剤中には、上記した如きノニオン性界面活性剤、含窒素アルカリ性化合物、pH調整剤、キレート剤及び有機溶媒以外に、通常この分野で用いられる試薬類を使用することができる。このような試薬類は、例えば配線のCuを保護し、Cuの腐食を防止する目的で用いられる、例えばヒドラジン又はその誘導体、

アスコルビン酸、蟻酸、ホルマリン等の還元剤、例えばベンゾトリアゾール又はその誘導体、チオ尿素類等の金属腐食防止剤等、半導体表面に対する洗浄剤の濡れ性を改善し、洗浄効果を向上させる目的で用いられる、ノニオン性界面活性剤以外の界面活性剤（例えばドデシルベンゼンスルホン酸等のアニオン系界面活性剤、アルキルトリメチルアンモニウム等のカチオン系界面活性剤、カルボキシベタイン等の両性界面活性剤等）等である。

【0106】これら試薬類は、通常この分野で使用される濃度範囲で用いればよい。例えば還元剤の使用量は、金属Cuの酸化を防止し得る量であればよく、通常0.01～5重量%、好ましくは0.05～1重量%である。また、金属腐食防止剤の使用量は、金属Cuと弱い結合を形成し、Cuに対する洗浄剤の溶解力を抑制し得る量であればよく、通常0.01～5重量%、好ましくは0.05～1重量%であり、ノニオン性界面活性剤以外の界面活性剤の使用量は、洗浄剤の表面張力を低下させ得る量であればよく、通常0.0001～1重量%、好ましくは0.001～0.1重量%である。

【0107】本発明の洗浄方法は、表面にCu配線が施された半導体表面を、上記した如き本発明の洗浄剤で処理すればよい。

【0108】表面にCu配線が施された半導体表面を、本発明の洗浄剤で処理する方法としては、通常この分野で行われる自体公知の半導体表面を洗浄する方法であればよく、具体的には、単に半導体を洗浄剤中に浸漬するディップ処理、半導体に洗浄剤をシャワー状に振りかける枚葉処理等の方法が挙げられる。

【0109】更に、本発明に於いては、洗浄時に物理的洗浄を併用することにより、より効果的にCuOを除去することができる。併用の具体的方法としては、表面にCu配線が施された半導体表面を、本発明の洗浄剤の存在下、物理的洗浄工程に付すこと等が挙げられる。

【0110】上記方法に於いて、本発明の洗浄剤を存在させる方法としては、具体的には、上記した如きディップ処理、枚葉処理等により本発明の洗浄剤を存在させた状態として物理的洗浄工程に付す方法等が挙げられる。また、物理的洗浄（工程）としては、例えば高速回転のポリビニルアルコール製ブラシ等を用いて半導体表面を洗浄するブラシスクラブ洗浄、高周波を用いるメガソニック洗浄等が挙げられる。

【0111】物理的洗浄を併用する場合のより具体的な手法としては、例えば半導体を本発明の洗浄剤中に浸漬した後、当該洗浄液中から取り出して半導体表面に当該洗浄剤を存在させた状態とした後に物理的洗浄を行う方法、半導体を本発明の洗浄剤中に浸漬させたまま物理的洗浄を行う方法、半導体表面に本発明の洗浄剤を振りかけて半導体表面に当該洗浄剤を存在させた状態とした後に物理的洗浄を行う方法、或いは半導体表面に本発明の洗浄剤を振りかけながら物理的洗浄を行う方法等が挙げ

られる。

【0112】ノニオン性界面活性剤を含む本発明の洗浄剤を用いた場合、銅配線を保護して洗浄液中に浮遊するスラリー由来のパーティクルや僅かにエッチングされた絶縁膜の滓等を寄せ付けないという効果が奏せられる。特に、四級アンモニウムとノニオン性界面活性剤とを含む本発明の洗浄剤を用いた場合には、四級アンモニウムによる絶縁膜のエッチングを低減することができ、銅配線を腐食することなくパーティクルを除去する効果が高い四級アンモニウムの利点を生かすことができ、そのため、絶縁膜のエッチングは最小限に抑えられ、表面荒れを起こすことがない。しかも、剥離した酸化銅の再吸着も有効に阻止される。

【0113】また、カチオン性、アニオン性または両性等のイオン性界面活性剤では、電氣的に半導体表面と結合して洗浄を妨げたり、本来アルカリ性で半導体表面と電氣的な反発をするスラリー由来のパーティクルの表面電荷を変化させ、パーティクルの再吸着を引き起こす場合がある。

【0114】以上のように、ノニオン性界面活性剤、特に分子中にアセチレン基を有するノニオン性界面活性剤、更にはこれと例えばアンモニア、一級乃至三級アミン又は四級アンモニウム等の含窒素アルカリ性化合物、なかでも特に四級アンモニウムの両者を含有する洗浄液で、銅配線を施した半導体表面を洗浄すれば、銅配線の腐蝕や酸化を起こさず、且つ表面荒れを起こすことなく、表面に吸着している不純物を除去でき、表面の清浄度を向上することができるという効果が特に顕著に奏せられる。

【0115】上記した如く、本発明の洗浄剤は、表面に銅配線が施された半導体表面の洗浄に極めて有用であるが、銅配線が施されたものに限らず、例えばアルミニウム配線やタングステン・プラグ等の銅以外の配線が表面に施された半導体表面の洗浄に於いても使用可能である。更にまた、本発明の洗浄剤は、半導体表面のみならず、プリント基板、LCD基板等の表面の洗浄にも使用し得る。

【0116】以下に実施例及び比較例を挙げるが、本発明はこれらにより何限定されるものではない。

【0117】尚、以下実施例で用いたノニオン性界面活性剤は、米国特許第3291607号に記載の方法に従い、対応するグリコール化合物とアルキレンオキサイドとの反応により合成できる。

【0118】また、本実施例及び比較例に於いて使用した熱酸化膜ウェーハ及び金属汚染ウェーハ、銅堆積ウェーハ、パーティクル汚染熱酸化膜ウェーハ及びパーティクル汚染銅堆積ウェーハは夫々以下の方法により調製したものを使用し、また、熱酸化膜ウェーハの酸化膜の膜厚、銅堆積ウェーハ表面の銅の膜厚、金属汚染ウェーハ表面に吸着残存している銅原子の吸着量（残存銅濃度）

及びパーティクル数は夫々以下の方法により測定した。

【0119】〔熱酸化膜ウェーハ〕4インチシリコンウェーハを、1%フッ酸水溶液で処理し、表面の自然酸化膜を除去した後、800℃で熱処理をし、ウェーハ表面に熱酸化膜（酸化ケイ素、絶縁膜）を形成したものを熱酸化膜ウェーハとした。尚、下記に示す方法により、当該熱酸化膜ウェーハの酸化膜の膜厚は、500Åであることを確認した。

【0120】〔金属汚染ウェーハ〕熱酸化膜ウェーハを、1ppmとなるように銅イオンを添加した硝酸水溶液に1分間浸漬し、超純水により10分間流水洗浄した後、スピン乾燥したものを金属汚染ウェーハとした。尚、下記に示す方法により、当該金属汚染ウェーハには、銅原子が 3×10^{14} 原子/cm² 吸着残存していることを確認した。

【0121】〔銅堆積ウェーハ〕熱酸化膜ウェーハ表面にスパッタリング法により金属銅を堆積させたものを銅堆積ウェーハとした。尚、下記に示す方法により当該銅堆積ウェーハ表面の銅の膜厚は、1000Åであることを確認した。

【0122】〔パーティクル汚染熱酸化膜ウェーハ及びパーティクル汚染銅堆積ウェーハ〕熱酸化膜ウェーハ又は銅堆積ウェーハを、夫々平均粒径0.2μmの3%アルミナスラリー水溶液に1分間浸漬し、超純水により10分間流水洗浄した後、スピン乾燥したものを夫々パーティクル汚染熱酸化膜ウェーハ又はパーティクル汚染銅堆積ウェーハとした。尚、下記に示す方法により、当該パーティクル汚染熱酸化膜ウェーハには、パーティクルが約850個/4インチウェーハ、パーティクル汚染銅堆積ウェーハには、パーティクルが約90個/4インチウェーハ夫々吸着残存していることを確認した。

【0123】〔酸化膜の膜厚測定法〕膜厚計（エリプソメータ）により測定した。

【0124】〔銅の膜厚測定法〕ウェーハを半分に割り、断面を電子顕微鏡により観察し、銅の膜厚を測定した。

【0125】〔銅原子吸着量（残存銅濃度）測定法〕ウェーハ表面に吸着残存した銅を、フッ酸-硝酸水溶液で溶解回収した後、該回収液中の銅濃度を、原子吸光法（黒鉛炉原子吸光分光分析装置）により測定した。得られた測定値に基づいて銅原子の吸着量（残存銅濃度）を求めた。

【0126】〔パーティクル数測定法〕ウェーハ表面に吸着残存しているパーティクルを表面異物検査装置（パーティクルカウンター）により測定した。

【0127】尚、本実施例及び比較例に於いては、特に断りのない限り濃度を表す%、ppm、ppbは全て重量比を示す。また、使用する水は全て超純水であり、銅が0.01ppb以下であることを確認してから使用した。

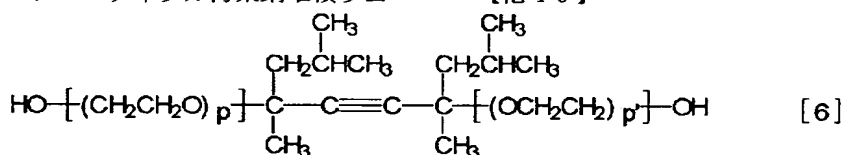
【0128】

【実施例】実施例1

超純水中にテトラメチルアンモニウムヒドロキシド（TMAH）を1%と、ノニオン性界面活性剤である下記一般式〔6〕で示され、オキシエチレン基の平均モル数〔p+p'〕が10であるジイソブチルジメチルブチンジオールポリオキシエチレングリコールエーテル

【0129】

【化49】



【0130】（以下、界面活性剤10と、略記する。）を0.03%溶解した洗浄剤（pH12以上）に、上記方法で作製した熱酸化膜ウェーハを60℃、10分間浸漬した。その後、ウェーハを引き上げ、超純水で10分間リンスし、スピン乾燥させた後、酸化膜の腐食の有無を確認するため、熱酸化膜ウェーハの酸化膜厚を測定した。結果を表1に併せて示す。

【0131】比較例1

超純水中にTMAHのみを1%溶解した洗浄剤（pH12以上）を用いた以外は、実施例1と同様の方法で熱酸化膜ウェーハを処理した後、熱酸化膜ウェーハの酸化膜厚を測定した。結果を表1に示す。

【0132】

【表1】

	添加剤 (添加量%)	pH	酸化膜厚 (Å)
実施例1	TMAH (1%) 界面活性剤10 (0.03%)	12以上	480
比較例1	TMAH (1%)	12以上	220

【0133】表1から明らかなように、本発明の洗浄剤（実施例1）は、熱酸化膜ウェーハの酸化膜厚に殆ど変

化を与えないこと、即ち、半導体表面の絶縁膜に悪影響を与えないことが判る。これに対し、四級アンモニウム

のみを含む従来の洗浄剤（比較例 1）は、酸化膜を著しく溶解或いはエッチングしていることが判る。

【0134】実施例 2

超純水中にノニオン性界面活性剤である上記一般式

〔6〕に於いてオキシエチレン基の平均モル数〔 $p + p'$ 〕が 12 であるジイソブチルジメチルブチンジオールポリオキシエチレングリコールエーテル（以下、界面活性剤 12 と、略記する。）を 0.001% 溶解した洗浄剤（ $pH 7$ ：中性溶液）に、上記方法で作製した金属汚染ウェーハを 60℃、10 分間浸漬した。その後、ウェーハを

【0135】比較例 2

超純水中にアニオン性界面活性剤であるドデシルスルホン酸ナトリウムを 0.001% 溶解した洗浄剤（ $pH 7$ ：中性溶液）を用いた以外は、実施例 2 と同様の方法で金属汚染ウェーハを処理した後、不純物（銅）除去能力を評価するため、金属汚染ウェーハ表面の銅原子吸着量（残存銅濃度）を測定した。結果を表 2 に併せて示す。

【0136】実施例 3

超純水中にコリンを 0.4% と、ノニオン性界面活性剤である上記一般式〔6〕に於いてオキシエチレン基の平均モル数〔 $p + p'$ 〕が 6 であるジイソブチルジメチルブチンジオールポリオキシエチレングリコールエーテル（以下、界面活性剤 6 と、略記する。）を 0.001% 溶解した洗浄剤（ $pH 12$ 以上）を用いた以外は、実施例 2 と同様の方法で金属汚染ウェーハを処理した後、不純物（銅）除去能力を評価するため、金属汚染ウェーハ表面

の銅原子吸着量（残存銅濃度）を測定した。結果を表 2 に併せて示す。

【0137】比較例 3

超純水中にコリンを 0.4% と、アニオン性界面活性剤であるドデシルベンゼンスルホン酸（ライオン社製）を 0.001% 溶解した洗浄剤（ $pH 12$ 以上）を用いた以外は、実施例 2 と同様の方法で金属汚染ウェーハを処理した後、金属汚染ウェーハ表面の銅原子吸着量（残存銅濃度）を測定した。結果を表 2 に併せて示す。

【0138】実施例 4

超純水中に TMAH を 0.03% と、ノニオン性界面活性剤である上記一般式〔6〕に於いてオキシエチレン基の平均モル数〔 $p + p'$ 〕が 8 であるジイソブチルジメチルブチンジオールポリオキシエチレングリコールエーテル（以下、界面活性剤 8 と、略記する。）を 0.001% 溶解した洗浄剤（ $pH 10.5$ ）を、上記方法で作製した金属汚染ウェーハにシャワー状に振りかけながら、1 分間、高速回転のポリビニルアルコール製ブラシでスクラブ洗浄した。その後、ウェーハを超純水で 10 分間リンスし、スピン乾燥させた後、不純物（銅）除去能力を評価するため、金属汚染ウェーハ表面の銅原子吸着量（残存銅濃度）を測定した。結果を表 2 に示す。

【0139】比較例 4

洗浄剤の代わりに超純水を用いた以外は、実施例 4 と同様の方法で金属汚染ウェーハを処理した後、金属汚染ウェーハ表面の銅原子吸着量（残存銅濃度）を測定した。結果を表 2 に併せて示す。

【0140】

【表 2】

	添加剤 (添加量%)	pH	残存銅濃度 (原子/cm ²)
実施例 2	界面活性剤 12 (0.001%)	7	1×10^{11}
実施例 3	コリン (0.4%) 界面活性剤 6 (0.001%)	12 以上	1×10^{10}
実施例 4	TMAH (0.03%) 界面活性剤 8 (0.001%)	10.5	5×10^9
比較例 2	ドデシルスルホン酸ナトリウム	7	9×10^{13}
比較例 3	コリン (0.4%) ドデシルベンゼンスルホン酸 (0.001%)	12 以上	8×10^{11}
比較例 4	無添加	7	2×10^{13}

【0141】表 2 から明らかなように、ノニオン性界面活性剤を含む本発明の洗浄剤（実施例 2）は、アニオン性界面活性剤のみを含む洗浄剤（比較例 2）に比較して金属汚染ウェーハ表面の残存銅濃度を著しく抑制し得、四級アンモニウムとアニオン性界面活性剤を含む洗浄剤（比較例 3）と比べても残存銅濃度を抑制し得ることが

判る。また、ノニオン性界面活性剤と四級アンモニウムとを含む本発明の洗浄剤（実施例 3）は、アニオン性界面活性剤のみを含む洗浄剤（比較例 2）及び四級アンモニウムとアニオン性界面活性剤を含む洗浄剤（比較例 3）と比較して、金属汚染ウェーハ表面の残存銅濃度を著しく抑制できることが判る。更には、化学的洗浄のみ

を行った場合（実施例 3）よりも、化学的洗浄と物理的洗浄を併用（実施例 4）した場合の方が、より効果的に、銅を除去し得ることが判る。

【0142】実施例 5

超純水中に TMAH を 3% と、ノニオン性界面活性剤である上記一般式 [6] に於いてオキシエチレン基の平均モル数 $[p + p']$ が 5 であるジイソブチルジメチルブチンジオールポリオキシエチレングリコールエーテル（以下、界面活性剤 5 と、略記する。）を 0.05% 溶解した洗浄剤（pH 12 以上）を用いた以外は、実施例 5 と同様 10

	添加剤 (添加量%)	pH	銅膜厚 (Å)
実施例 5	TMAH (3%) 界面活性剤 5 (0.05%)	12 以上	1000
比較例 5	ジエタノールアミン (3%)	10	150

【0145】表 3 から明らかなように、本発明の洗浄剤である、ノニオン性界面活性剤と四級アンモニウムを含む洗浄剤（実施例 5）は、銅堆積ウェーハ表面の銅膜厚に殆ど影響をあたえないことから、銅を溶解やエッチング等しないことが判る。これに対し、二級アミンは含むもののノニオン性界面活性剤を含まない洗浄剤（比較例 5）は、銅を著しく溶解或いはエッチングしていることが判る。

【0146】実施例 6

【0148】（以下、界面活性剤 6-2 と、略記する。）0.03% を溶解した洗浄剤（pH 9）に、上記方法で作製したパーティクル汚染熱酸化膜ウェーハ及びパーティクル汚染銅堆積ウェーハを、1MHz の高周波を印可しながら、60℃ で 10 分間浸漬した。その後、ウェーハを引き上げ、超純水で 10 分間リンスし、スピン乾燥させた後、不純物（パーティクル）除去能力を評価するため、パーティクル汚染熱酸化膜ウェーハ及びパーティクル汚染銅堆積ウェーハのパーティクル数を測定した。結果を表 4 に示す。

【0149】比較例 6

	添加剤 (添加量%)	pH	パーティクル数 (個/μm ²)	
			パーティクル汚染熱酸化膜ウェーハ	パーティクル汚染銅堆積ウェーハ
実施例 6	TMAH (0.03%) 界面活性剤 6-2 (0.03%)	9	30	5
比較例 6	TMAH (0.03%) 塩化ステアリルジメチルアンモニウム (0.03%)	9	1200	202

【0151】表 4 から明らかなように、本発明の洗浄剤 50 であるノニオン性界面活性剤と四級アンモニウムを含む

の方法で銅堆積ウェーハを処理した後、銅堆積ウェーハの銅膜厚を測定した。結果を表 3 に併せて示す。

【0143】比較例 5

超純水中にジエタノールアミンを 3% 溶解した洗浄剤（pH 10）を用いた以外は、実施例 5 と同様の方法で銅堆積ウェーハを処理した後、銅堆積ウェーハの銅膜厚を測定した。結果を表 3 に併せて示す。

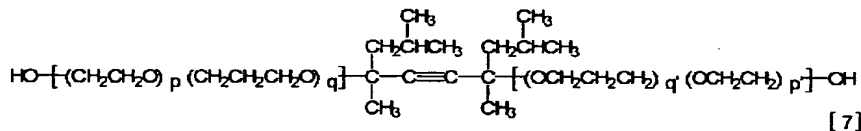
【0144】

【表 3】

超純水中に TMAH を 0.003% と、ノニオン性界面活性剤である下記一般式 [7] で示され、オキシエチレン基の平均モル数 $[p + p']$ が 6 であり、オキシプロピレン基の平均モル数 $[q + q']$ が 2 であるジイソブチルジメチルブチンジオールポリオキシプロピレンポリオキシエチレングリコールエーテル

【0147】

【化 50】



超純水中に TMAH を 0.003% と、カチオン性界面活性剤である塩化ステアリルジメチルアンモニウムを 0.03% 溶解した洗浄剤（pH 9）を用いた以外は、実施例 6 と同様の方法でパーティクル汚染熱酸化膜ウェーハ及びパーティクル汚染銅堆積ウェーハを処理した後、パーティクル汚染熱酸化膜ウェーハ及びパーティクル汚染銅堆積ウェーハのパーティクル数を測定した。結果を表 4 に併せて示す。

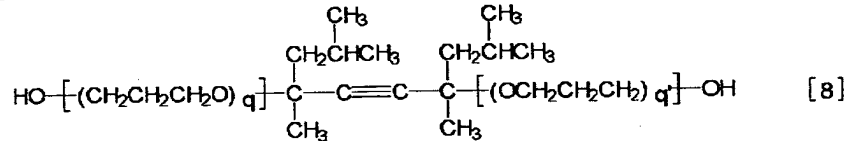
【0150】

【表 4】

洗浄剤（実施例 6）は、熱酸化膜ウェーハ表面に吸着残存するパーティクル数が 30、銅堆積ウェーハ表面に吸着残存するパーティクルが 5 であり、いずれの場合もパーティクル除去効果が著しく高いことが判る。これに対して、カチオン性界面活性剤と四級アンモニウムを含む洗浄剤（比較例 6）は、熱酸化膜ウェーハ表面に吸着残存するパーティクル数が 1200、銅堆積ウェーハ表面に吸着残存するパーティクルが 202 であり、いずれの場合もパーティクル除去効果が低いことが判る。

【0152】実施例 7

超純水中にアンモニアを 3% と、ノニオン性界面活性剤である上記一般式〔6〕に於いてオキシエチレン基の平均モル数〔p + p'〕が 4 であるジイソブチルジメチル



【0155】を 0.05% 溶解した洗浄剤（pH 10）を用いた以外は、実施例 7 と同様の方法で銅堆積ウェーハを処理した。

【0156】

【発明の効果】以上の如く、本発明は銅配線が施された

ブチンジオールポリオキシエチレングリコールエーテルを 0.05% 溶解した洗浄剤（pH 11）に、上記方法で作製した銅堆積ウェーハを室温（25℃）で 30 分間浸漬した。その後、ウェーハを引き上げ、超純水で 10 分間リンスし、スピン乾燥させた。

【0153】実施例 8

超純水中にジエタノールアミンを 3% と、ノニオン性界面活性剤である下記一般式〔8〕で示され、オキシプロピレン基の平均モル数〔q + q'〕が 4 であるジイソブチルジメチルブチンジオールポリオキシプロピレングリコールエーテル

【0154】

【化 51】

半導体表面に吸着残存する不純物を除去でき、且つ銅配線を腐蝕及び酸化したり、表面荒れを起こすことなく、半導体表面の洗浄を行うことが出来る方法を提供するものであり、本発明の洗浄液を用いれば、半導体製造時における諸問題を解決できる。

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